

Synthesis of chain-like carbon nano- onions for application in room temperature volatile organic chemical gas sensors



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BSc (MSc)

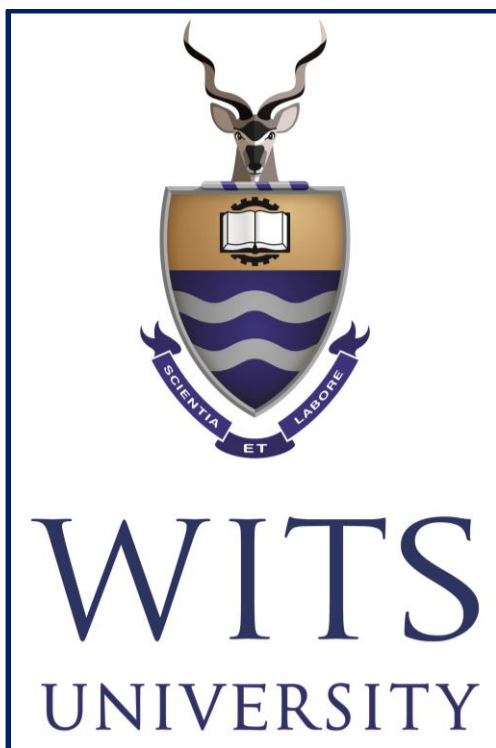
This Thesis was submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfillment for the degree of **Doctor of Philosophy in Chemistry** (Material Sciences).

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DECLARATION

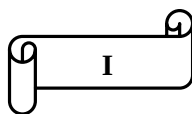
I declare that this Thesis is hereby submitted for the degree of **Doctor of Philosophy** in the Faculty of Science under the School of Chemistry at the University of the Witwatersrand is my own unaided work and has not been submitted for examination at any institution.



A handwritten signature in black ink, appearing to read 'Mongwe', is positioned above a horizontal dashed line.

Thomas Hlamalani Mongwe

On this 21st day of September 2021



DEDICATION

This work is a special dedication to my beloved family:

- My parents: Mr. Y.S Mongwe and Ms. J.S Skhosana, My brother:
E.N Mongwe
- My late grandparents: Mr. J.S.A Mongwe, Mrs. E.M Mongwe, Mr.
J.B Skhosana, Mr. M.S Skhosana and Mrs. F.N Skhosana
- My late great grandparents
- My wife: Mrs. F.N Mongwe, My son: N.O.N Mongwe

“I have spent most of my family time doing this research trying
contribute in the scientific knowledge, for your patience granted me
strength”.

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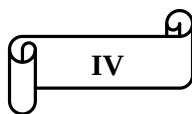
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Proverbs 18:15:

“The mind of the prudent acquires knowledge, and the ear of the wise seeks knowledge”.



PUBLICATIONS, PRESENTATIONS AND AWARDS

Publications during the PhD study period (2018-2021)

- Boitumelo J. Matsoso, Clara I. Garcia-Martinez, **Thomas H. Mongwe**, Bérangère Toury, José P.M. Serbena, Catherine Journet. *Chemical sensing properties of BaF₂-modified hBN flakes towards detection of volatile organic compounds*. Chemosensors, 9 (2021); 263. DOI: <https://doi.org/10.103390/chemosensors9090263>
Author's contribution: Participated in development of the analyte detection technical method, data analysis (i.e. Chemiresistive data analysis) as well as in the sequence alignment and grammar/language correction during the writing process of the manuscript.
- Boitumelo J. Matsoso, Clara I. Garcia-Martinez, **Thomas H. Mongwe**, Bérangère Toury, José P.M. Serbena, Catherine Journet. *Room temperature solid-state ammonia vapor detection on hBN nanosheets*. Journal of Physics: Materials, 4 (2021); 044007. DOI: <https://doi.org/10.1088/2515-7639/ac09d4>
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- Themba D. Ntuli, **Thomas H. Mongwe**, Ludwe L. Sikeyi, Orlette Mkhari, Neil J. Coville, Edward N. Nxumalo, Manoko S. Maubane-Nkadimeng. *Removal of hexavalent chromium via an adsorption coupled reduction mechanism using olive oil derived carbon nano-onions*. Environmental Nanotechnology, Monitoring and Management. 16 (2021); 100477. DOI: <https://doi.org/10.1016/j.enmm.2021.100477>
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- Annah Makhongoana, Boitumelo J. Matsoso, **Thomas H. Mongwe**, Neil J. Coville, Daniel Wamwangi, Manoko S. Maubane-Nkandimeng. *The role of oxygen in a carbon source*

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- Ludwe L. Sikeyi, Themba D. Ntuli, **Thomas H. Mongwe**, Nobanathi W. Maxakato, Emanuela Carleschi, Bryan P. Doyle, Neil J. Coville, Manoko S. Maubane-Nkandimeng. *Microwave assisted synthesis of nitrogen doped and oxygen functionalized carbon nano-onions supported palladium nanoparticles as hybrid anodic electrocatalysts for direct alkaline ethanol fuel cells*. *International Journal of Hydrogen Energy*. 46 (2021); 10862-10875. DOI: <https://doi.org/10.1016/j.ijhydene.2020.12.154>

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- Bokome Shaku, Thapelo P. Mofokeng, **Thomas H. Mongwe**, Neil J. Coville, Kenneth I. Ozoemena, Manoko S. Maubane-Nkandimeng. *Physicochemical properties of nitrogen doped carbon nano-onions grown by flame pyrolysis from grapeseed oil for use in supercapacitors*. *Electroanalysis*. 32 (2020); 2946-2957.

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- Lebogang R. Mosiane, Boitumelo J. Matsoso, Annah Makhongoana, Bridget K. Mutuma, **Thomas H. Mongwe**, Neil J. Coville, Manoko S. Maubane-Nkadimeng. *Tuning the properties of CVD-grown multiwalled carbon nanotubes by ex situ codoping with boron and nitrogen heteroatoms*. *Journal of Nanoparticle Research*. 21 (2019); 1-15.

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- **Thomas H. Mongwe**, Boitumelo J. Matsoso, Bridget K. Mutuma, Neil J. Coville, Manoko S. Maubane. *Synthesis of chain-like carbon nano-onions by a flame assisted pyrolysis techniques using different collecting plates*. Diamond and Related Materials. 90 (2018); 135-143. DOI: <https://doi.org/10.1016/j.dia mond.2018.10.002>
- **Thomas H. Mongwe**, Themba D. Ntuli, Ludwe L. Sikeyi, Neil J. Coville, Messai A. Mamo, José P.M. Serbena, Manoko S. Maubane-Nkadimeng. *The use of ex-situ nitrogen doped olive oil-derived carbon nano-onions for application in chemiresistive gas sensors to detect acetone at room temperature*. (Recently **submitted** for publication)
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- **Thomas H. Mongwe**, Neil J. Coville, Messai A. Mamo, José P.M. Serbena, Manoko S. Maubane-Nkadimeng. *The selective study of response and recovery times of acetone and ammonia room temperature gas sensors fabricated using nitrogen doped carbon nano-onions/manganese oxide nanorods composite*. (**To be submitted** for publication)
- **Thomas H. Mongwe**, Neil J. Coville, Messai A. Mamo, José P.M. Serbena, Manoko S. Maubane-Nkadimeng. *The study of functionalized carbon nano-onions and their metal oxide-containing composite for application in chemiresistive gas sensors*. (**To be submitted** for publication)

Research presentations and visits

- NanoAfrica 2018 conference: Poster presentation “*Facile synthesis of carbon nano-onions*”, Durban (April 2018).
- CoE-SM/AMSEN annual student presentation: Poster presentation “*Synthesis of carbon nano-onions and their application in photovoltaic cells*”, Johannesburg (April 2018).
- Wits Cross Faculty 2018 Symposium: Poster presentation “*Facile synthesis of chain-like carbon nano-onions for application in room temperature gas sensors*”, Johannesburg (October 2018).
- CoE-SM/AMSEN annual student presentation: Oral presentation “*Production of carbon nano-onions for application in gas sensors using a cost effective method*”, Johannesburg (May 2019).
- Wits Science Slam: Oral presentation “*The novel use of carbon nano-onions and sun rays to generate electricity*”, Johannesburg (July 2019)
- Organic Optoelectronic Devices group meeting: Oral presentation “*Detection of different analytes using a low frequency operated chemiresistive gas sensor*”, Curitiba, Brazil (September 2019).
- MSSA 2019 conference: Oral presentation “*Characterization of chain-like carbon nano-onions using electron microscopy and other related techniques*”, Cape Town (December 2019).
- Wits Cross Faculty 2020 Online Symposium: Oral presentation “*The use of olive oil flame-derived carbon nano-onions for the detection of ethanol at room temperature*”, Johannesburg (October 2020).
- National Young Chemists’ 2021 Online Symposium: Poster presentation “*The significant use of carbon nano-onions as one of carbon allotrope for improving our lifestyle*”, Cape Town (July 2021).
- Visiting student researcher at Federal University of Parana, Curitiba, Brazil in Prof. Serbena’s optoelectronics laboratory. September - November 2019.

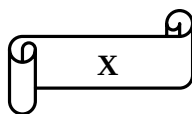
Academic awards

- Received first prize for poster presentation, and received a poster presentation certificate: CoE-SM/AMSEN annual student presentation, Johannesburg (April 2018).
- Received a poster presentation certificate: Wits Cross Faculty 2018 Symposium, Johannesburg (October 2018).
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- Received an oral presentation certificate: Wits Science Slam, Johannesburg (July 2019).

ABSTRACT

This study reports on the use of chain-like carbon nano-onions (CLCNOs) in volatile organic chemical (VOC) sensors. The discoveries made in this work suggests a possible inexpensive route to fabricate gas detectors that can be used to monitor and/or reduce toxic VOCs in the environment. It was found that, the properties of CLCNOs can easily be tuned by functionalization, heteroatom doping and by varying the synthesis parameters. The facile synthesis of quasi-spherical CLCNOs was achieved using a flame pyrolysis method that allowed for the formation of carbon nanoparticles and manganese dioxide nanorods (MONRs) based composites. CLCNOs were easily synthesized using four combustible oils; (1) coconut oil, (2) cod liver oil, (3) olive oil and (4) sweet oil as carbon sources. Functionalization of CLCNOs was achieved by refluxing the materials in H_2O_2 . CLCNOs were successfully doped with nitrogen using ammonia and pyridine as nitrogen sources using a chemical vapour deposition (CVD) and open flame pyrolysis (OFP) processes respectively. Microscopy data showed that the multi-layered CLCNOs exhibited particle sizes less than 80 nm. Additionally, the TGA results confirmed that the OFP produces cleaner (i.e. no traces of metal impurities) and thermally stable CLCNOs in gram scale as compared to other conventional methods (e.g. CVD and arc-discharge). It was observed that the defect densities of doped and functionalized CLCNOs increased as compared to the as-synthesized CLCNOs. Moreover, XPS results confirmed successful doping and functionalization of CLCNOs. Hence, the as-synthesized, doped and fictionalized CNOs portray varying chemical properties depending on their surface characteristics such as the presence of different types of nitrogen atoms and/or carboxylic groups.

On the other hand, a hydrothermal method was used to synthesize metal oxide nanorods (MONRs). The synthesized CLCNOs and MONRs were analysed using various analytical techniques (e.g. electron microscopy and Raman spectroscopy) to study their chemical and physical characteristics. CLCNOs-MONRs-based composite were prepared along with polyvinylpyrrolidone (PVP) and the sensors were used at room temperature (i.e. 25 °C). The PVP was used to stabilize the MONRs for low temperature use. Different state-of-the-art basic sensing devices were fabricated to explore their detection ability towards acetone, ammonia, chloroform, ethanol, and toluene. Interestingly, different CLCNOs/MONRs/PVP composites presented variable dynamic and static characteristics when used in chemiresistive gas sensors fabrication. Different gas sensors showed a great significance of CLCNOs in the composite since they allowed for better electron transport in the sensing layer. A synergistic property was realized between the three materials (i.e. CLCNOs,



MONRs and PVP) used in the gas sensing composite layer. Higher signals and/or positive responses were observed for most devices used to detect various VOCs at selected concentrations (in ppm) and operating frequencies (≤ 10 kHz). The investigations also revealed that most sensors were capable of detecting different VOCs depending on the chemical interaction between the VOC and the sensing material. As such, this study presents the use of different CLCNOs/MONRs/PVP composites as gas sensing materials at room temperature.

Thus, the findings in this project play a role in the development of gas sensors operated at low frequencies and temperature. Furthermore, this study contributes towards the knowledge of using cost effective electronic devices given less electrical power consumption needed by low frequency operated devices presented herein.

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LIST OF ABBREVIATIONS AND NOMENCLATURE

Abbreviation	Description
BCP	Brass collecting plate
BET	Branauer-Emmett-Teller
CB	Carbon black
CHN	Carbon, Hydrogen, Nitrogen
CLCNOs	Chain-like carbon nano-onions
CNFs	Carbon nanofibers
CNMs	Carbon nanostructured materials
CNOs	Carbon nano-onions
CNTs	Carbon nanotubes
CH ₃ COCH ₃	Acetone
CH ₃ CH ₂ OH	Ethanol
CH ₃ Cl	Chloroform
C ₅ H ₅ N	Pyridine
C ₆ H ₅ CH ₃	Toluene
CCVD	Catalytic chemical vapour deposition
CVD	Chemical vapor deposition
DMF	Dimethylformamide
DTA	Differential thermogravimetric analysis
EDS	Energy dispersive X-ray spectroscopy
EDX	Energy dispersive X-ray
FDW	First-order derivative weight loss
FP	Flame pyrolysis
FTIR	Fourier Transform Infrared spectroscopy
FWHM	Full width at half maximum
H ₂ O	Water
H ₂ O ₂	Hydrogen peroxide
HMTEM	High magnification transmission electron microscopy
IDE	Inter-digitated electrode
KMnO ₄	Potassium permanganate
LCR	Inductance, Capacitance and Resistance

LoD	Limit of detection
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	Manganese sulphate
MONRs	Manganese dioxide nanorods
MO	Metal oxide
N-CLCNOs	Nitrogen-doped carbon nano-onions
N-HCS	Nitrogen doped hollow carbon spheres
NIOH	National Institute of Occupational Health
NH_3	Ammonia
OFF	Open flame pyrolysis
PS	Pore sizes
RH	Relative humidity
SA	Surface area
SCNMs	Spherical carbon nanomaterials
SEM	Scanning electron microscopy
SNR	Signal to noise ratio
STC	Standard test condition
TEM	Transmission electron microscopy
TCC	Toxic chemical compounds
TGA	Thermo-gravimetric analysis
PXRD	Powder X-ray diffraction
PAH	Polycyclic aromatic hydrocarbon
PVP	Polyvinylpyrrolidone
VOC	Volatile organic chemical
VOCGS	Volatile organic chemical gas sensor
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy

CHAPTER 1

Synopsis

1.1. Introduction

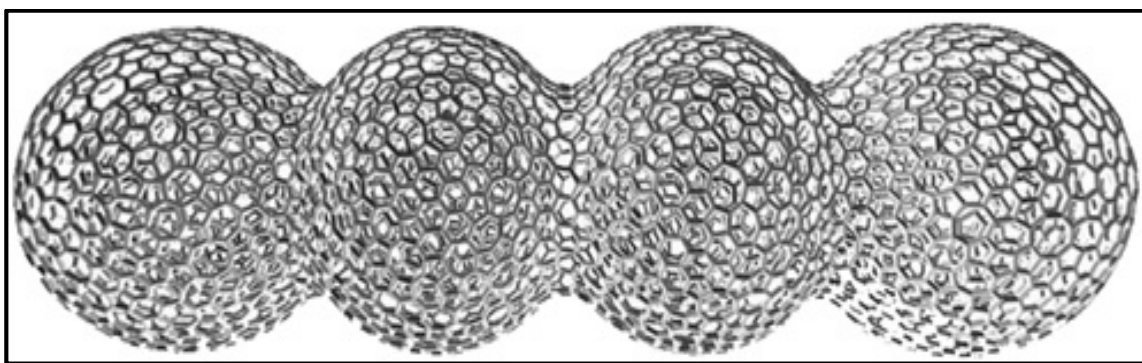
1.1.1. A brief background and motivation towards the study

Volatile organic chemicals (VOCs) such as ethanol, propanone, acetone and toluene are harmful chemical gases constantly emitted by various industries [1-2]. The presence of most VOCs (e.g. toluene) in the living environment beyond 0.5 mg/m^3 or 0.113 ppm limit can lead to human health related issues such as central nervous system dysfunction [3]. Therefore, it is imperative that precise and rapid alerting, detection and monitoring of toxic chemical gases be available to minimize and/or prevent accidents involving explosions or serious poisoning (i.e. health hazards). This can be achieved partly by implementing specific gas sensors to detect the gases prior to their build up to unacceptable levels. The VOCs can be detected by a chemical gas sensor that follows the photoelectric principles which can either involve catalytic combustion or an electrochemical method [4].

A chemical gas sensor is a device that systematically transforms chemical information to a useful analytical signal and normally consists of two functions, i.e., a *receptor* function which identifies or recognizes a chemical substance, and a *transducer* function which transduces the chemical signal into an output signal of the sensor [5, 6]. Depending on the nature of the sensing device (i.e. whether is electrochemical or thermoelectrical), the device can positively either use n- or p-type sensing material [7]. The commonly used sensing films are mainly made of oxides of readily available metals such as zinc and other transition metals [7-9]. However, these metal oxide-based sensors pose a number of unpleasant characteristics, such as high cross-sensitivity and operation temperature, long-term signal drift, sensitivity to humidity and slow sensor response. To overcome this, carbon nanomaterials (e.g. carbon nanotubes) and polymers (e.g. poly(p-phenylenevinylene)) are normally introduced to achieve better sensing characteristics such as improved sensitivity [10]. However, these also suffer from high fabrication costs, selectivity and the flexibility to work at room temperature [9, 10]. As such, in order to improve metal oxide-based sensor performance, a

series of gas sensors fabricated using semiconducting metal oxides (e.g. manganese dioxide (MnO_2)) based hybrids/nanocomposites have been studied [9, 10]. One way to achieve this, is through the incorporation of inexpensive carbon nanomaterials (e.g. carbon nano-onions) and selected non-conducting polymer(s).

Carbon nanomaterials such as carbon spheres and carbon dots have been explored as composite materials for detecting volatile organic chemicals [11, 12]. Among the family of spherical carbon nanomaterials, carbon nano-onions exhibit interesting chemical and physical properties that are advantageous for their application in gas sensing devices [13, 14]. The discovery of carbon nano-onions (CNOs) by Iijima revealed that this material has been used in many applications (e.g. batteries and solar cells) [15-20]. CNOs have structural morphologies ranging from polyhedral to quasi-spherical nanostructured materials with particles sizes that are less than 100 nm [21, 22]. One of the commonly used method for the synthesis of CNOs is the catalytic chemical vapor deposition method [23]. However, researchers such as Dubey and Mohapatra together with their co-workers recently reported a facile synthetic method for producing CNOs [24, 25]. Their laboratory method involved the use of a flame assisted process (i.e. flame pyrolysis) which allowed them to synthesize aggregated or conglomerated CNOs, herein named as chain-like carbon nano-onions (CLCNOs) as shown in **Figure 1.1** [24, 25]. Interestingly, this is a catalyst free method which makes use of combustible hydrocarbons (e.g. wood wool, diesel, lycopene (from tomato) and petrol (gasoline)) as carbon sources to form CLCNOs in the gram scale [26, 27].



Scheme 1.1: Structural model of chain-like CNOs [28].

It is best known that CLCNOs exhibit unique electrical, catalytic, mechanical and optical properties which makes them interesting candidates for discovering and exploring a new

generation of low-power consumption, down sized, omni-presented and wearable sensors [29]. This can eventually allow the design of room-temperature operated gas sensors that are able to detect traces of different air and environmental pollutants [30]. On the other hand, research has shown that the properties of CLCNOs can be improved/alterd through doping or functionalization [31, 32]. Moreover, doping or functionalization of CLCNOs introduces heteroatoms or organic functional groups in their structural matrix, providing their long-term operation stability through alteration of both their chemical and physical properties [33]. In this project, the use of different CLCNOs-based MONRs composites that can offer an alternative route for fabricating various VOCs sensors was investigated experimentally. Additionally, a non-conducting polymer was selected for its use as a MONRs nanoparticles stabilizer allowing for the detection of VOCs at room temperature to avoid working at elevated temperatures (i.e. >100 °C).

1.2. Purpose of the study

1.2.1. Research question

What are the significant physicochemical properties that need to be exhibited by CLCNOs for their use as an active nanomaterial for a room temperature VOC gas sensing nano-composite composed of MONRs and polyvinylpyrrolidone?

1.2.2. Hypotheses

The proposition for this study is that upon using the functionalized CLCNOs-metal oxide nano-composite/hybrid, the working capacity of the sensors will be improved when compared to those using only metal oxides. Moreover, introduction of heteroatoms in the structural matrix of the CLCNOs will increase the electrical properties of the materials resulting in improved sensing abilities of the sensing devices containing this nanomaterial composite.

1.3.3. Aim of the study

The aim of this study is to discover and fundamentally explore the synthesis along with functionalization of CLCNOs using a simple synthesis procedure followed by their characterization for application in room temperature VOC gas sensing devices or systems.

1.3.4. Objectives of the study

- (a) To use a simple catalyst free, oil-wick (flame pyrolysis) method for the production of CLCNOs.
- (b) To investigate the factors affecting the morphology and particle sizes of CLCNOs by: -
 - (i) Using different readily available organic oils (e.g. coconut oil, cod liver oil, olive oil and sweet oil (from Hercules Company)).
 - (ii) Using different metal collecting plates (e.g. brass, copper, zinc and steel).
 - (iii) Using different distances between the open flame and each CLCNO collecting plate.
 - (iv) Using a radical diluting gas (Ar) along with controlled amounts of oxygen.
- (c) To investigate the effect of high heat treatments/annealing ($\sim 1000\text{ }^{\circ}\text{C}$) on the properties of the CLCNOs.
- (d) To ascertain and optimize the physiochemical properties of the CLCNOs for gas sensing purposes by: -
 - (i) Doping CLCNOs produced with heteroatoms (i.e. nitrogen atoms (ex-situ and in-situ nitrogen doping)).
 - (ii) Functionalizing CLCNOs with carbonyl functional groups.
 - (iii) Mixing CLCNOs with rarely used metal oxide (i.e. MnO_2)
- (e) To fabricate VOC gas sensing devices using optimized conditions of CLCNOs mixed with metal oxide and polymers (i.e. application of CLCNOs/MONRs/polyvinylpyrrolidone composite).
- (f) To perform gas sensing measurements/tests using different VOCs (i.e. acetone, ammonia, chloroform, ethanol, and toluene) to test the gas sensing properties of CLCNOs and/or its composite(s) in the sensing device.

1.3. Organization of the thesis

Chapter 1

This chapter gives a brief background and motivation towards the study which is accompanied by the purpose of the study. The research question, hypothesis, aim and objectives of this study are given with the purpose of the study.

Chapter 2

In this chapter, a brief background on: toxic volatile organic chemicals, volatile organic chemical gas sensors, carbon based nanomaterials (including carbon nano-onions) and their various synthesis routes, carbon based nanoparticles doping and functionalization as well as composites formation, carbon nano-onions application in volatile organic chemical sensors (i.e. chemiresistive gas sensors) is presented.

Chapter 3

This is the chapter in which the analysis, characterization and measuring or testing techniques that were used in this study are described in detail.

Chapter 4

In this chapter, a brief understanding of chain-like carbon nano-onions (CLCNOs) formation is discussed. The use of coconut oil, cod liver oil, olive oil and sweet oil as different carbon precursors used in the flame pyrolysis process to generate CLCNOs is further explored. Thus, this follows the investigated open flame pyrolysis method for its use to synthesize CLCNOs with different chemical and physical properties.

Chapter 5

The presentation of an extensive study based on the basic gas sensing application of CLCNOs derived from the selected oil (i.e. olive oil) is given in this chapter. In this study, the discussion on the use of CLCNOs-based composite with manganese oxide and a non-conductive polyvinylpyrrolidone as a volatile organic chemicals (VOCs) gas sensing composite is given. Moreover, the VOCs of interest are; acetone, chloroform, ethanol, and toluene.

Chapter 6

This chapter discusses the synthesis of CLCNOs using the flame pyrolysis method and the ex-situ doping of CLCNOs. The investigation on the effect of different ammonia flow rates used during doping is further discussed in which the gas sensing behavior of the sensing composites that were made from pristine and nitrogen doped CLCNOs are explained.

Chapter 7

In this chapter, a report on an extensive study that is based on the application of in-situ doped carbon nano-onions in gas sensors is presented. The use of pyridine as the carbon source as well as the doping agent is to synthesize nitrogen doped CLCNOs is explained. Moreover, the application of nitrogen doped CLCNOs in chemiresistive gas sensors for detecting acetone, ethanol and toluene is explained. Herein, further discussions are given following the dynamic and static characteristics of the sensing devices achieved through chemiresistive measurements.

Chapter 8

This chapter presents a study that gives discussions based on the response and recovery times of acetone and ammonia. Two different gas sensing composites were studied through the dynamic characterization in order to understand the basic sensing behavior of the two VOCs used.

Chapter 9

In this chapter a report on the functionalization of CLCNOs using hydrogen peroxide is presented. A discussion on MnO_2 is used with functionalized CLCNOs (f-CLCNOs) as an active gas sensing material for application in chemiresistive gas sensors is given in this chapter. Thus, the dynamic and static characterizations are also presented following the results obtained after testing the sensing behavior of a gas sensing composite that contains f-CLCNOs/MONRs/PVP at room temperature.

Chapter 10

This chapter provides the general conclusions and future prospects that emanated from the study.

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CHAPTER 2

Literature review

2.1. Background and introduction

The expansion of human activities increasingly contributes to the major release of various toxins which directly affect the living environment as well as different living organisms. Notably, there has been concerns raised about the release of toxic volatile organic chemicals (VOCs) by various industries in different production fields. The VOCs are the most harmful and toxic pollution gases and are extremely detrimental to ecological harmony and human health. They can bring irritation to different body parts such as eyes, respiratory tracts and skin. They can also cause some lung related diseases that can arise from particulate matter formed when the VOC(s) molecules interact with other air pollutants such as oxides of nitrogen or sulphur to form NO_x or SO_x [1].

For example, unreasonable farming management in the agricultural field has caused a majority of the outdoor release of nitrogen that is sourced from ammonia. This has then induced an urgent necessity of sensitive monitoring of nitrogen in the environment and involved targeting its source (e.g. from ammonia and other nitrogen based VOCs). Hence, the National Institute for Occupational Safety and Health (NIOSH) in various countries has established recommended exposure limits for specific VOCs. Among the various low dose VOCs detection technologies, chemiresistive sensors prevail over their electrochemical optical and mass-sensitive counterparts due to the distinct merits of handy measurement, easy fabrication and high cost-effectiveness [2-9].

2.1.1. Volatile organic chemicals

The World Health Organization (WHO), as well as many health organizations in countries (e.g. National Institute of Occupational Health (NIOSH) in South Africa), are concerned with illnesses caused by indoor and outdoor air pollutants [10]. These pollutants include organic chemical compounds which are chemicals that mainly contain hydrocarbon based molecules. Many of these volatile organic chemicals such as acetone, ammonia, chloroform, ethanol, methanol and toluene are regarded as toxic chemical compounds (TCCs) when exposed to living organisms depending

on their amount of exposure (see **Figure 2.1**). Toxic chemical compounds directly contribute to indoor and outdoor air pollution since they evaporate easily at room temperature due to their high vapor pressures or low boiling points.

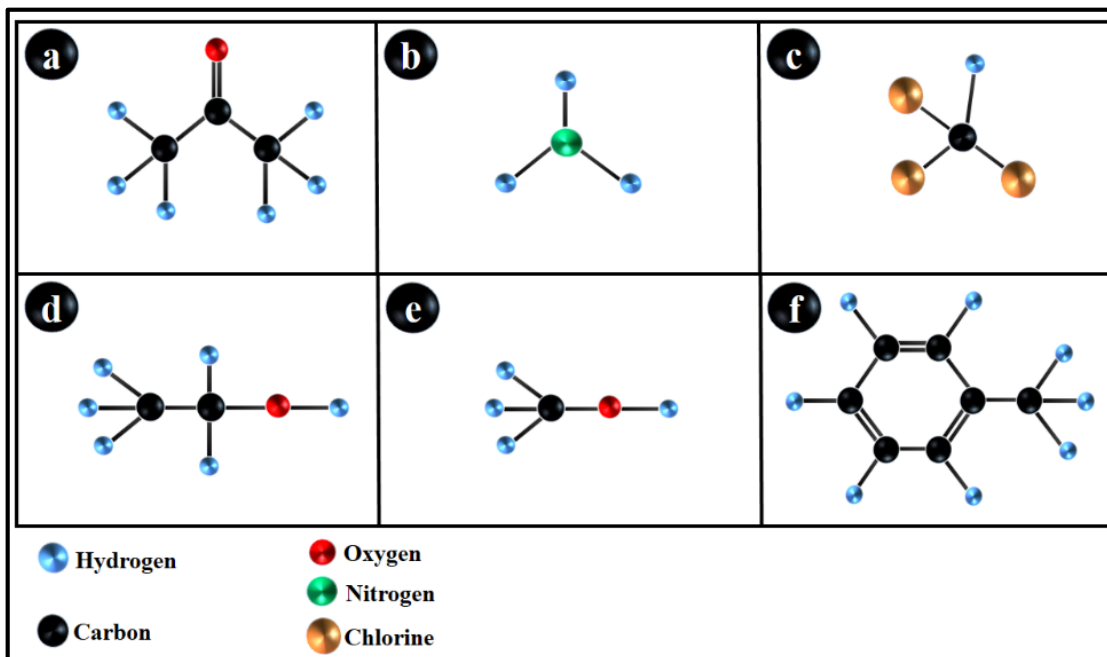


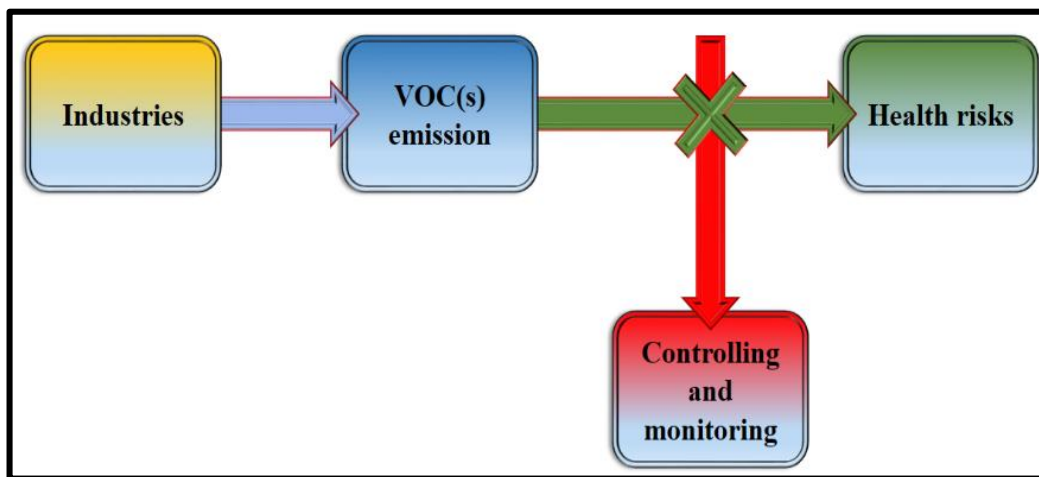
Figure 2.1: The structure of different VOCs (a) acetone, (b) ammonia, (c) chloroform, (d) ethanol, (e) methanol, and (f) toluene [11-22].

They are mostly classified as carcinogenic irritants and/or toxicants. These TCCs can be released from various industries including the automotive and food industries. Materials such as cleaning agents, cosmetics, fabrics, food packaging as well as various paints are examples of items that are used on a daily basis and often generate VOCs [23]. Hence, the direct emission of VOCs from various anthropogenic and biogenic sources introduces negative health effects to all living organisms due to communal VOCs exposure (see **Table 2.1**) [24]. It is important to note that VOCs containing open-chain hydrocarbons including alcohols, aldehydes, esters and ketones are generally found above ground level as well as above the sea level [25, 26]. For example, acetone can be found as an indoor and/or outdoor toxic air pollutant and it can be emitted or generated from different sources including personal care products (e.g. nail polish removers and perfumes) as well as from organic solvents used in different industries [27-29].

Table 2.1: Gives examples of common sources of specific VOCs and their uses.

VOC	Examples of common sources and uses
Acetone	Plants
	Biofuels
Ammonia	Riparian vegetation
	Fertilizers
Chloroform	Oceans
	Chemical industries
Ethanol	Automotive or petrochemical industries
	Automotive fuels
Methanol	Synthetic chemical industries
	Synthetic fuels
Toluene	Chemical industries
	Paint thinners

Due to continuous anthropogenic and biogenic activities, solutions to VOCs emissions has been sought for the past decade [30, 31]. This problem can be monitored by involving the use of chemical gas sensors in order to reduce health risks posed by the exposure of living organisms towards different VOCs [32]. To avoid alarming health risks, various chemical gas sensors have been applied to control and/or monitor the emission of VOCs in various areas (see **Scheme 2.1**).

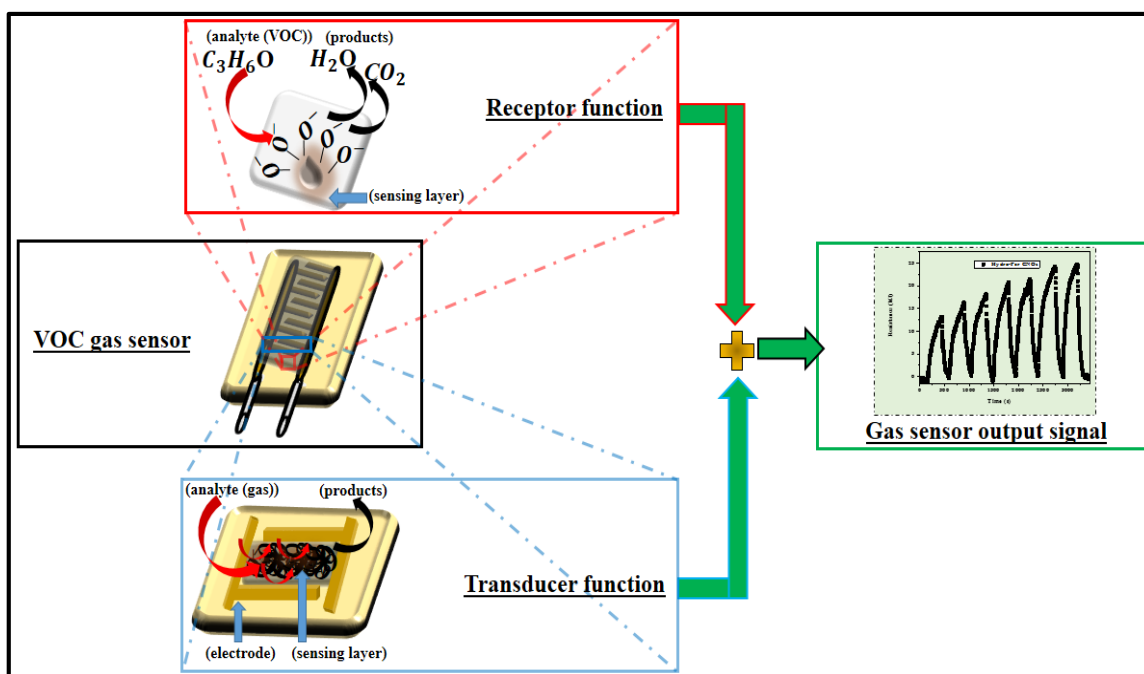


Scheme 2.1: An example of volatile organic chemicals emission chain.

Chemical gas sensors have been commercialized to detect different VOCs that are commonly found as indoor and/or outdoor toxic chemicals [10, 33]. In summary, VOCs are regarded as an omni-present environmental pollutant that can be associated with domestic health risks (e.g. increased human mortality) encountered by the general public around the world.

2.1.2. Toxic chemical or volatile organic chemical gas sensors and their fundamental working principle and/or gas sensing mechanism

Since VOCs are useful in industries such as in the automotive fuel industry, and in many biomedical applications. They will continue to be used even though they are harmful to human lives. Thus, different VOCs concentrations remain monitored using various gas sensors in most industries. A VOC gas sensor is a systematic device that transforms volatile organic compound information to a useful analytical signal.



Scheme 2.2: General gas sensing functions (i.e. receptor and transducer) of a sensor fabricated with a sensing layer that contains oxygen species [38, 39].

There are generally two types of sensors, called active and passive sensors [34]. The active sensor generates a signal in response to an external stimulus directly. In this case, the conversion of the input stimulus signal into output energy is achieved without any additional power source [35].

However, an external energy or power source is required in the case of a passive sensor for their standard operation whereby the signal obtained is modified by the sensor to produce a useful output signal [36]. Hence, their electrical properties usually changes in response to an external stimulus. Normally, a sensor consists of two functions namely; (1) the *receptor* function which is responsible for the identification of a chemical compound, and (2) the *transducer* function which later transduces the given chemical signal into an output signal of the sensor following the specific recognition of the chemical compound (see **Scheme 2.2**) [37].

The physicochemical properties of the sensing material is important for both the receptor and transducer functions. Usually, redox reactions occur in the receptor function depending on the stoichiometry of the sensing material. The adsorption and/or desorption parameters can involve the crystallite faceting of the sensing material nanoparticles [40]. Surface additives, including dopants, also play a significant role in the reaction. In turn, the transducer function involves the mobility of the concentrated charge carriers in the crystallite network of the sensing material and this can depend on the grain size [41].

Over the past decades, different gas sensors have been fabricated using different materials and methods that are based on the variation of electrical properties e.g. as seen in metal oxide semiconductor based gas sensors [42]. The electrochemical gas sensors (e.g. metal semiconductor, catalytic combustion and solid electrolyte sensors) are one of the other types of gas sensors that have been developed to monitor toxic gases in domestic and industrial environments [43]. The electrochemical gas sensors can be regarded as sensors that utilize their electrical properties. The sensors can differ in terms of their sensing methods and they can be divided into two groups involving; (a) electrical property variations (e.g. gas sensors) and (b) other property variations (e.g. acoustic or optical sensors) [44]. Numerous electrochemical gas sensors may have limited sensing abilities and these properties can depend on the materials used during their fabrication. The sensor limitations are normally in terms of their selectivity, sensitivity, and stability which are the important 3-S parameters. The crucial 3-S parameters contribute to every sensing device performance in which the selectivity of the sensor is defined as the ability to discriminately identify the target gas molecules from other molecules within the sensing system that contains the sample [45]. Moreover, when dealing with a literal interpretation of a single sensor, selectivity can be expressed as the specificity of the sensing device that only identifies the target gas molecules.

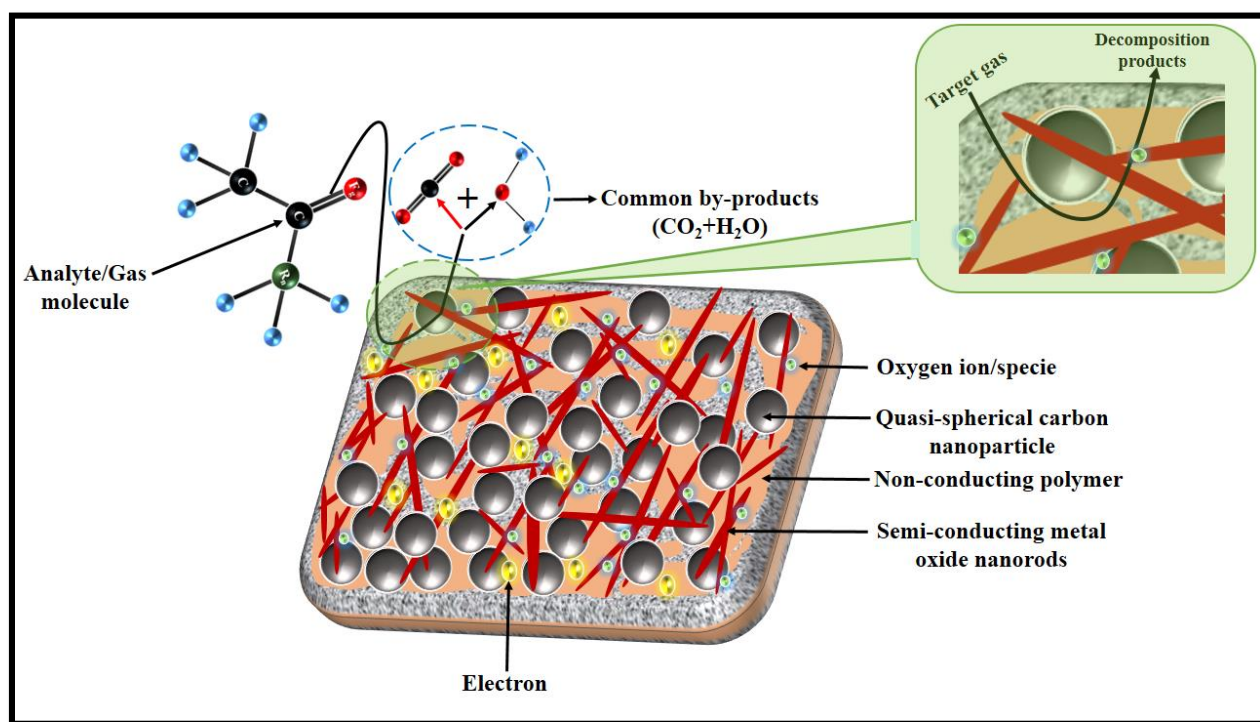
Therefore, the sensitivity of a gas sensor can be defined as the sensor's ability or capability to discriminately identify small variances in terms amount by mass or concentration of the target gas molecules that are in the sensing system. Hence, it can be regarded as the slope of the calibration curve in which the range of the concentration of the standard solution measured for the given calibration curve includes the dynamic range and the one in which the signal is linearly proportional to the concentration is best known as the linear range [46]. Thus, the stability of the sensor is its capability to produce repeatable outputs for the same environment over a monitored period. Every sensing device can be subjected to stability tests by repeating measurements over a certain period or multiple circles of its exposure to the target gas molecules. Hence, such processes will allow for clearing concerns around the device stability by investigating issues relating to possible sources that might contribute to the detector's instability (e.g. drifts, hysteresis, and irreversibility) [47, 48]. As such, it is worthwhile to note that there are numerous factors that contribute to these kind of limitations. For example, the semiconductor metal oxide gas sensors may have active sensing material dopants and/or surface impurities that can affect the selectivity of the sensor [49].

Moreover, factors that affect the sensitivity of a sensor also include humidity, dopants, grain size and the porosity of the microstructure that is used as the sensing material [50, 51]. The stability of a semiconductor metal oxide gas sensor can be affected by bulk diffusion, changes in humidity and temperature, electrical contact degradation, phase and structural transformation, as well as the active sensing material poisoning [51]. Thus, possible solutions to the factors involving costs and efficiency problems of toxic chemical gas sensors (TCGSs) could be provided by the use of inexpensive carbon nanostructured materials (CNMs) along with different inexpensive metal oxides (e.g. MnO_2). The use of CNMs when fabricating TCGSs could improve the accessibility and usage of the TCGSs. Effective implementation could decrease the health related issues (e.g. chronic cancers/respiratory diseases) caused by these toxic gases.

One of the commonly sought-after type of VOC gas sensors is the electrochemical gas sensor known as the chemiresistive gas sensor. Hence, this study focuses on this type of chemiresistive gas sensor as a systematic device that can positively transform volatile organic compound information into a useful analytical signal. At room temperature most VOCs are not very reactive and exhibit high chemical stability which makes it difficult to detect them using a single polymer or metal oxide based gas sensor [52]. Notably, most of the single polymer or metal oxide based

chemiresistive gas sensor operate at elevated temperature and not at room temperature in which the gas sensitive material (e.g. single polymer or metal oxide) is exposed to various atmospheric air compositions. The electrical characteristics of chemiresistive gas sensor does not only change as a result of targeted molecular interactions (at elevated temperatures) but it also changes because of other or external gases that are present in the atmosphere [53, 54].

The physicochemical characteristics of the VOC are known to affect the electrical characteristics and/or parameters of the sensing material [55]. If the sensing material is composed of a semiconducting material (e.g. MnO_2) that forms the receptor layer, there will be a gradual loss of the sensitivity, caused by the irreversible adsorption of trace impurities in the atmosphere, in a process called “poisoning”. When poisoning occurs, the surface active sites are hindered or bind to the atmospheric impurities and the electrical parameters, as a function of time, drift resulting in poor long-term stability of the chemiresistive gas sensor [55, 56].



Scheme 2.3: General gas sensing mechanism model of a sensor fabricated with a carbon-based semiconducting material and a non-conducting polymer.

Generally, the gas sensing mechanism involves the adsorption of gas molecules (e.g. ethanol molecules) by the active sensing surface in two ways; (1) chemisorption and (2) physisorption. They are both involved during the adsorption of gas molecules. A chemical reaction occurs between the active sensing surface and the targeted gas molecules (i.e. analyte) which is then followed by the charge carriers (i.e. electron) transference during chemisorption [57, 58]. The active sensing surface can be made of carbon-based semiconducting material and a non-conducting polymer on which both chemisorption and physisorption can occur as depicted in **Scheme 2.3** [57, 58]. Chemisorption involves an endothermic process in which the heat of the chemical adsorption (i.e. activation energy) can be thermally supplied (see **Figure 2.2**) [59-61]. During chemisorption, if the adsorbed oxygen molecules are charge carrier acceptors, the conductivity of the chemiresistive gas sensor increases but it will decrease when the adsorbed oxygen molecules donates charge carriers [61]. In gas sensing studies, the gas can either be classified as an oxidizing gas (i.e. electron acceptors) or a reducing gas or (i.e. electron donor). Depending on the sensing material' type (i.e. n- or p-type), gases such as nitrogen dioxide, hydroxyethane or ethanol can be regarded as reducing gases respectively [62].

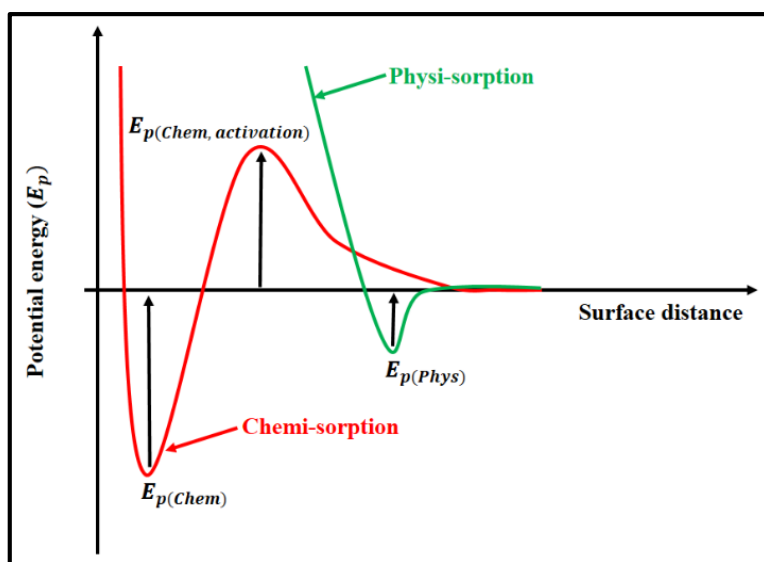


Figure 2.2: The potential energy diagram illustrating the difference between the chemisorbed and physisorbed chemical species [60].

The n-type semiconductors have electrons as the majority charge carriers which decreases the conductivity (i.e. increases the resistance) in the presence of an oxidizing gas. In contrast, the

interaction with a reducing gas increases the conductivity (i.e. decreases the resistance) due to a depletion of electrons. Positive charges are the majority charge carriers in the p-type semiconductors which leads to the decrease in conductivity (i.e. increase in resistance) upon interaction with a reducing gas. When an oxidizing gas introduces positive charges into the active sensing material layer, the concentration of negative charge carriers will be reduced resulting in increased conductivity (i.e. decrease in resistance) [63].

In fact, the first step of the interaction of adsorbed oxygen molecules with an active sensing surface is called physisorption. Physisorption predominantly occurs at low temperature since it involves an exothermic process [58, 64]. In this process, adsorption takes place through weak physical bonding which includes dipole-dipole interactions and Van der Waals forces [64, 65]. However, the energy required during chemisorption is higher than that required for the physisorption process. Hence, to fulfill the energy demand for the chemical reactions, chemiresistive gas sensors based on either single-polymer or metal oxide are commonly operated at elevated temperature, especially for volatile organic compounds since they show a low chemical reaction rate at room temperature. In practical terms, adsorption occurs through physisorption (followed by chemisorption) for which a much smaller energy of activation is needed [66].

Following multiple studies on the gas sensing mechanisms, a model for understanding the sensing mechanism can be elaborated upon by using the mathematical description given by the Langmuir adsorption isotherm. This isotherm was developed by Irving Langmuir in 1916 and the method focused on the occupied and un-occupied sites of the active sensing material [67, 68]. Actually, the gas sensing mechanism is very complex and not fully understood and, there are points that are still missing for purposes of understanding the detection of VOCs by various sensing materials. Hence, investigating metal oxide composite gas sensors can be very helpful to clarify VOC detection at room temperature. Additionally, a sensing device fabricated using metal oxide composites is able to convert a variation of any property and quantity of the input signal into a readable and interpretable output signal.

The characteristics of an ideal gas sensor should include high VOC selectivity and sensitivity, long term reliability and stability, short recovery and response times, good signal-to-noise ratio and a complete reversibility behavior. Moreover, the gas sensor needs to be flexible, inexpensive,

portable, and simple (i.e. with minimal complexity) while exhibiting multiplexing capabilities. These additional factors allows for detection of various VOC(s) concentrations which can be generally determined using **Formula 2.1** [69-72].

$$C(\text{ppm}) = \frac{2.46 V_{\text{ad}} \rho_a}{V_c M_{\text{wa}}} \times 10^7 \dots\dots\dots [2.1]$$

Where V_{ad} represents the volume of the added analyte (i.e. volume of VOC in μL) into the analysis or testing chamber, V_c is the volume of the analysis chamber measured in mL, ρ_a is the density of analyte in $\text{g}(\text{mL})^{-1}$ and M_{wa} is the molecular weight of analyte in $\text{g}(\text{mol})^{-1}$.

The reliability, selectivity and sensitivity of a gas sensor are the characteristics that are active sensing material dependent. On the other hand, the response and recovery times as well as the noise are more complex features since there exist multiple components in a gas sensor. It is imperative to note that in a gas sensing system, the main source of noise is the system itself since all other electronic components contribute to the output noise. Thus, it is important to shield multiple noise sources within the gas sensing system.

The gas sensor's response can be calculated from the output value before the measurement is started (i.e. R_0) and the value measured in the measurand presence (R_{meas} , see **Formula 2.2**).

$$\left| \frac{\Delta R}{R_0} \right| = \left| \frac{R_{\text{meas}} - R_0}{R_0} \right| \dots\dots\dots [2.2]$$

The changes in frequency of a sensor can be observed considering the strength of the blank signal divided by the background noise of the blank signal over the same time, and this is known as the signal-to-noise ratio (SNR or S/N) given by **Formula 2.3** [73].

$$\text{SNR} = \frac{\text{Signal}}{\text{Noise}} = \frac{\mu}{\sigma} \dots\dots\dots [2.3]$$

Where μ is the signal mean or expected value and σ is the standard deviation of the noise given out by each sensor. The SNR can alternatively be defined as the ratio of the strength of the signal plus noise carrying information to the unwanted interference. If this ratio is equal to zero, then it

will be difficult to measure the gas sensor's signal directly. Thus, sophisticated signal processing techniques can be employed to measure the desired gas sensor's signal.

Therefore, the sensitivity (S_s) and the limit of detection (LoD) can be calculated using **Formulae 2.4** and **2.5** respectively. The change in the sensor response per concentration unit of the analyte (i.e. the slope (linear fit) of a calibration curve) determines the sensitivity of a gas sensing device. This can be the first derivative of its response (herein; the response R is the relative resistance variation $R = \Delta R/R_0$), with respect to the concentration of the analyte, at any concentration on the response curve [74, 75].

$$S_s = \frac{\partial(\frac{\Delta R}{R_0})}{\partial[C_a]} \dots\dots\dots [2.4]$$

Where, the change in resistance is given by $\Delta R = R_a - R_0$ in which R_a is the resistance of the sensor when exposed to analyte, R_0 is the resistance of the sensor in an inert atmosphere (e.g. under N_2) or background gas and $[C_a]$ is the concentration of the analyte. Moreover, the lowest amount of analyte in the detection system that can be detected and that is significantly different from the blank, but not necessarily quantitated under stated experimental conditions can also be estimated. This can be achieved by using the LoD formula (see **Formula 2.5**) where X_b is the mean response of the blank and σ_b is the standard deviation of the blank [76, 77].

$$LoD = X_b + 3\sigma_b \dots\dots\dots [2.5]$$

Lastly, the time interval for the gas sensor's response (i.e. R_{meas}) to change from 10 to 90% of its final saturation value (i.e. R_f) after applying the stimulation as a step-function is given as the sensor's response time. In the case of a reversible system, it is then possible to also identify the time for the response signal to change from 90 to 10% of R_f which is then regarded as the recovery time of the gas sensing system (see **Figure 2.3**) [78].

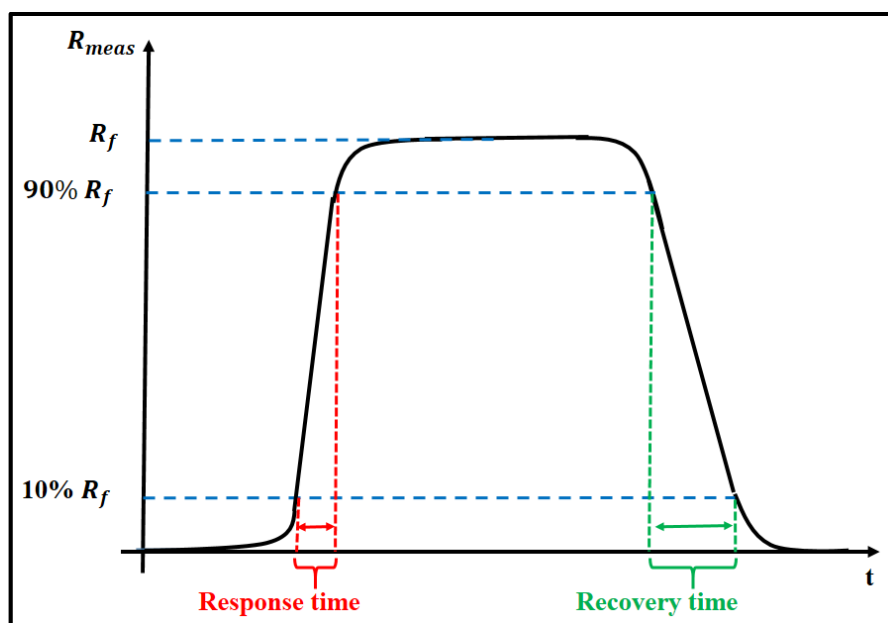


Figure 2.3: General plot of the response and recovery time of a chemical gas sensor following the stimulation as a step-function [78].

2.1.3. Black carbon nanoparticles and carbon nano-onions

Engineers and scientists have been interested in the combustion processes of different hydrocarbons to generate thermal energy or carbonaceous materials. The combustion of hydrocarbon oils can produce a black carbonaceous powder (BCP) which can be used in different applications. The general application of BCPs includes their use as colour in printing inks and a reinforcing agent for rubber (e.g. in automotive tire manufacturing) [79]. The BCP product can be formed by different flame pyrolysis processes (FPP). Similarly, carbon black (CB) can be produced through the FPP and the product is comparable to BCP in terms of its physicochemical properties [80, 81]. Unfortunately, CB nanoparticles are often confused with those of soot and other derivatives such as BCP, even though they contain more than 97% of elemental carbon with a minimal quantity of other elements and chemical compounds [82-85]. It is also to be noted that the black carbon particles are capable of adsorbing harmful polycyclic-aromatic hydrocarbons (PAHs) such as naphthalene onto their surfaces. Thus, toxic VOCs can be adsorbed on carbon surfaces, depending on the type of carbonaceous particulates involved [86, 87].

Carbon nanoparticles produced through combustion usually forms by nucleation processes from species such as PAHs and radicals (ions) via different growth and/or nucleation processes [88-94].

During the pyrolysis process, the formation of carbon particles usually involves formation of reactive radicals that nucleate and aggregate into aromatic carbon rings of different molecular shapes and sizes. Stable intermediates are later formed with relatively strong carbon sp^2 hybridised covalent bonds and the extra stability afforded by aromatic rings [95]. The reaction proceeds until polycyclic aromatic hydrocarbons (PAHs) are formed and they further accrete to form carbon lattices along with the formation of quasi-spherical multi-layered carbon nanoparticles [95, 96]. This follows the suggestion made by Homann and Wegner in 1967 whereby they proposed that the role of the polyacetylenes as well as the polycyclic aromatics in the process of particles inception is important for the carbon nucleation as described by **Equation 2.1** [97].



The carbon nucleation process is capable of forming spherical carbon nanostructured materials (SCNMs) exhibiting good electrical, mechanical and physiochemical properties [98]. SCNMs such as carbon dots, carbon spheres, and carbon nano-onions (CNOs) have been used in numerous applications such as catalysis, energy, and sensing or storage devices [98, 99]. Interestingly, the discovery of fullerenes in 1985 marked the beginning of the current carbon nanoscience revolution [100, 101]. The unique all-carbon structure of closed-cage molecules or fullerenes has also attracted considerable attention from diverse scientific fields ranging from materials science to medicinal chemistry because of their electronic properties and nanometre dimensions. Reports on fullerenes further lead to scientific discussions based on multi-shelled fullerenes simultaneously with CNTs and these equally fascinating all-carbon molecules have received much attention over time [98, 102].

In 1980 Iijima discovered the carbon allotrope commonly known as carbon nano-onions (i.e. multi-shelled fullerenes) which has a quasi-spherical and/or polyhedral nanostructured morphology with particle sizes less than 100 nm [103, 104]. They were initially observed as a byproduct in carbon black synthesis. This report was followed by their first observation by Ugarte when he subjected amorphous carbon nanoparticles to an electron beam by irradiation [105-108].

Lately, carbon nano-onions (CNOs) have become an important SCNMs because of their unusual chemical and physical properties that relate to their unique morphology [109]. They were termed carbon nano-onions due to their cross sectional appearance which exhibits concentric multi-layers

similar to those of an onion. Following the report made by Heidenreigh, Hess, and Ban, it can be said that CNOs are also made of short-range ordered curved graphitic layers with different diameters that form quasi-spherical shapes to create a quasi-spherical multi-layered nanomaterial as shown in **Figure 2.4** [110, 111].

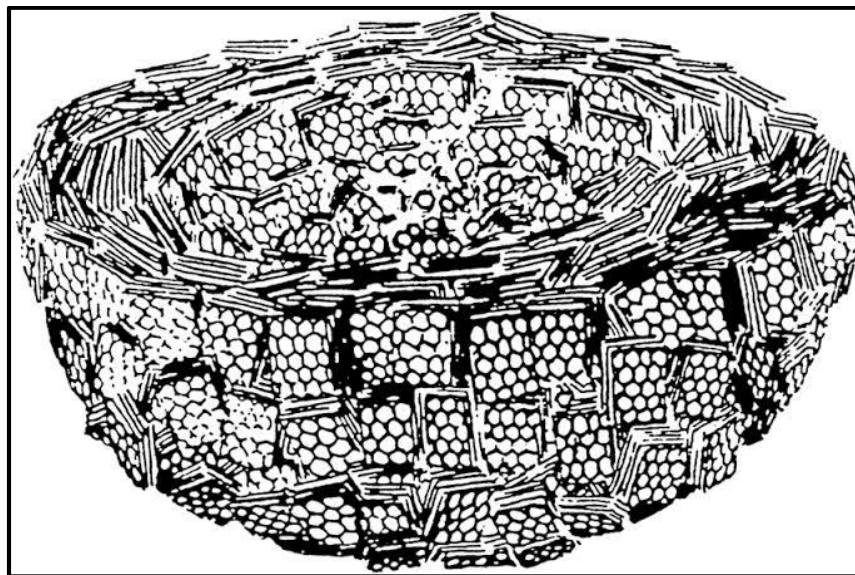


Figure 2.4: An example of short-range ordered curved graphitic layers forming a quasi-spherical shape of a carbon nanoparticle [110].

Moreover, the CLCNOs nanoparticles can be connected to each other i.e. in a chain-like linkage, as shown in the structural description shown in **Figure 2.5**. Different synthesis methods and/or pathways lead to CLCNOs with differing physical properties as a result of a change in core type (metallic core filled, hollow and solid), and the number of shells (layering) [112-119]. CLCNOs preparation methods can be classified into two broad categories, namely; chemical and physical methods [120]. The chemical methods (e.g. chemical vapor deposition) include the catalytic pyrolysis reactions of various hydrocarbons, catalytic disproportionation of different carbon sources as well as formation via hydrocarbon explosions. In the other case, the electric arc discharge and laser ablation methods are among the physical synthesis methods that can be used to synthesize CLCNOs [120] This suggests that the precursor (i.e. hydrocarbon source) used for their synthesis also governs the type of CLCNOs that form.

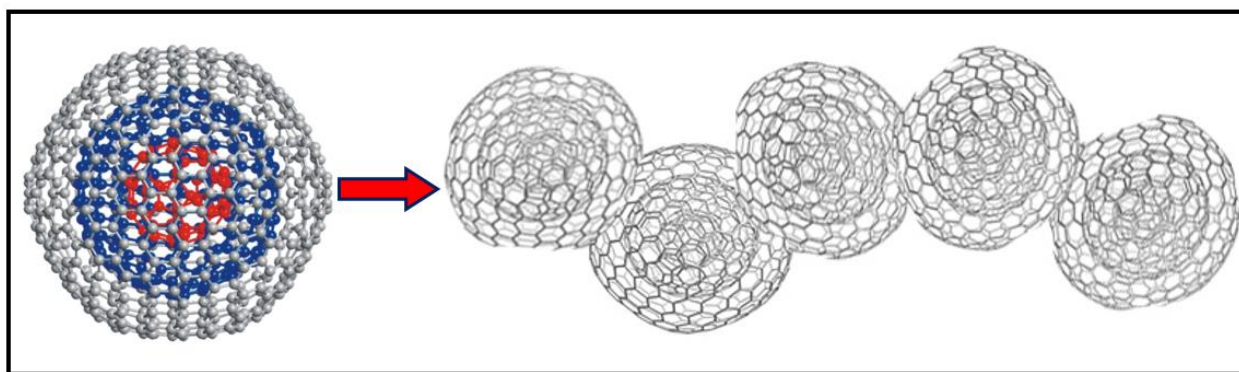


Figure 2.5: The chain-like linkage connection of CLCNOs nanoparticles [121, 122].

Recently, researchers such as Dubey *et al.*, and Mohapatra *et al.*, reported a facile synthetic method for producing CLCNOs using a flame assisted CLCNOs process (i.e. flame pyrolysis) [123, 124]. This is a catalyst free method which makes use of combustible hydrocarbons (e.g. wood wool, diesel, lycopene (from tomato) and petrol (gasoline)) as carbon sources to form CLCNOs in the gram scale [125-127]. The formation of CLCNOs solely relies on the availability of polyaromatic hydrocarbons (PAHs) which form carbon and hydrogen radicals that react to form concentric fullerene-like shells following a process similar to that of snow accretion [95, 128]. Different hydrocarbons (e.g. vegetable oils) usually produce CLCNOs with comparable particle sizes. Interestingly, the shell layering, graphitic nature, interlayer spacing and structural morphology of CLCNOs produced can be tuned by annealing processes [129].

2.1.4. Doping and functionalization of carbon nano-onions

Most studies report on different carbon allotropes that are doped with different heteroatoms including nitrogen [130]. The nitrogen doped carbon nanostructured materials (N-CNMs) have been used in various applications such as in sensors [130-135]. Various applications of N-CNMs are possible since nitrogen atoms are capable of adding electrons to CNMs. Electrical conductivity properties usually emerge as a result of effective structural matrix modulation due to the extra π -electrons in the graphitic plane of the N-CNMs. Additionally, the electronegativity difference between carbon ($\chi = 2.5$) and nitrogen ($\chi = 3.0$) gives rise to different structural properties. The N-doped carbons exhibit larger amounts of n-type carriers in the graphitic carbon as well as generate a high surface energy [136]. These properties also contribute to positive catalytic reactivity, energy conversion, and other flexible electronics effects [137].

The hetero-atomic doping processes of CNMs can be categorized into two types; in-situ and ex-situ doping [138]. The in-situ and ex-situ doping processes result in extrinsic and/or intrinsic heteroatom additions to the CNMs structural matrix in which different types of carbon to nitrogen bonds can be formed (e.g. pyridinic-N, pyrrolic-N) [139]. The heteroatom in-situ doping involves the direct introduction of heteroatoms into the as-synthesized carbon nanoparticles structural matrix in which the carbon (e.g. hydrocarbon oils or C_2H_2) and heteroatom precursor (e.g. NH_3) are simultaneously used for heteroatom addition into the CNMs structural matrix [138, 140]. In the ex-situ doping process, the heteroatom precursor is separately and step-wise added into as-synthesized CNMs [141].

The most commonly used dopants (i.e. heteroatoms) include boron (B), nitrogen (N), sulphur (S), fluorine (F) and phosphorus (P). In the case of nitrogen doping, the common process of doping CNMs with nitrogen involves the use of acetonitrile and ammonia [142]. These doping precursors (i.e. acetonitrile and ammonia) can either be used for in-situ and ex-situ doping. Thus, the in-situ or ex-situ doping process can be used to dope CLCNOs in order to modify the physicochemical properties such as electrical conductivity and structural durability or strength [143-145].

Apart from heteroatom doping (e.g. N-doping), the as-prepared CLCNOs can further be structurally modified by using different functionalization processes which involves well-designed organic synthesis techniques. The functionalization process can be used to improve the dispersibility of CLCNOs in both organic and aqueous solvents. CLCNOs functionalization can further improve the surface areas of the carbons that alternatively provides increases the miscibility for their full potential to be realized in multiple applications [146]. During CLCNOs functionalization, multiple non-covalent interactions are important for forming multiple hydrogen bonds along with Van der Waals interactions. Different synthetic pathways (i.e. functionalization processes) are also capable of providing covalent surface functionalization that can also increase the CLCNOs dispersibility [146]. When methods such as the Hummers' method are used, CLCNOs can be functionalized with carboxyl groups to create CLCNOs chemically bonded to carboxylic (i.e. $COOH$) groups [98, 147]. This type of functionalization offers CLCNOs the ability to interact or react with other functional compounds to form supramolecular architectures [148].

2.1.5. The formation of carbon nano-onions composite with metal oxides and/or polymers

Generally, CNMs can be interesting candidates to add to and improve metal oxide-based sensor performance due to their unique electrical, catalytic, mechanical and optical properties [149-151]. It is expected that CLCNOs will be good candidates for application in VOC gas sensing systems. They exhibit unique and tunable chemical and physical properties with the added advantage that they can be produced at low cost. Their application with respective metal oxides can be used to develop a new generation of low-power, downsized, and omni-presented sensors [152, 153]. It was previously reported in the literature that there is a common synergistic interaction between carbon and various transition metal oxides when used for different applications such as in catalysis of oxygen reduction reaction as well as in electrochemical sensing [154-158].

Among transitional metal oxides, manganese dioxide (i.e. MnO_2) offers n-type semiconducting behavior when compared to Mn_2O_3 at ambient conditions [159]. The advantages of its use includes chemical stability, eco-friendliness, inexpensiveness, low toxicity, natural abundance and tunable structural morphologies [160-162]. Julien *et al.*, reported that MnO_2 can be found in different morphologies such as nanoneedles, nanorods, nanotubes and nanowires which can be used for various applications (e.g. rechargeable batteries and electrocatalysis) as shown in **Figure 2.6** [163, 164]. Moreover, they can be synthesized using different wet chemical methods such as hydrothermal method, sol-gel and the thermal reflux method [165-167]. Unfortunately, MnO_2 has various drawbacks including its low electrical conductivity which is dependent on its polymorphic state (e.g. α -, β -, γ - and δ - MnO_2) [168-170]. However, it has also been reported that various carbonaceous materials' electrical properties can be synergistically improved by MnO_2 due to the high porosity, larger surface area, structural flexibility and their stability [171, 172]. Alternatively, mixing carbonaceous material with MnO_2 to make a carbon-metal oxide composite can enhance the active sites, increase the electric conductivity (i.e. improve the lost electrical capacity), improve the homogeneity of electrochemical reaction, and reduce the ionic resistance of the MnO_2 [173, 174]. Thus, a carbon to metal oxide composite (e.g. CLCNOs- MnO_2) is an interesting material that can be used to fabricate and produce small and wearable chemical gas sensors that could eventually allow the design of room-temperature operated gas sensors that are able to detect traces of air pollutants such as different VOCs [175].

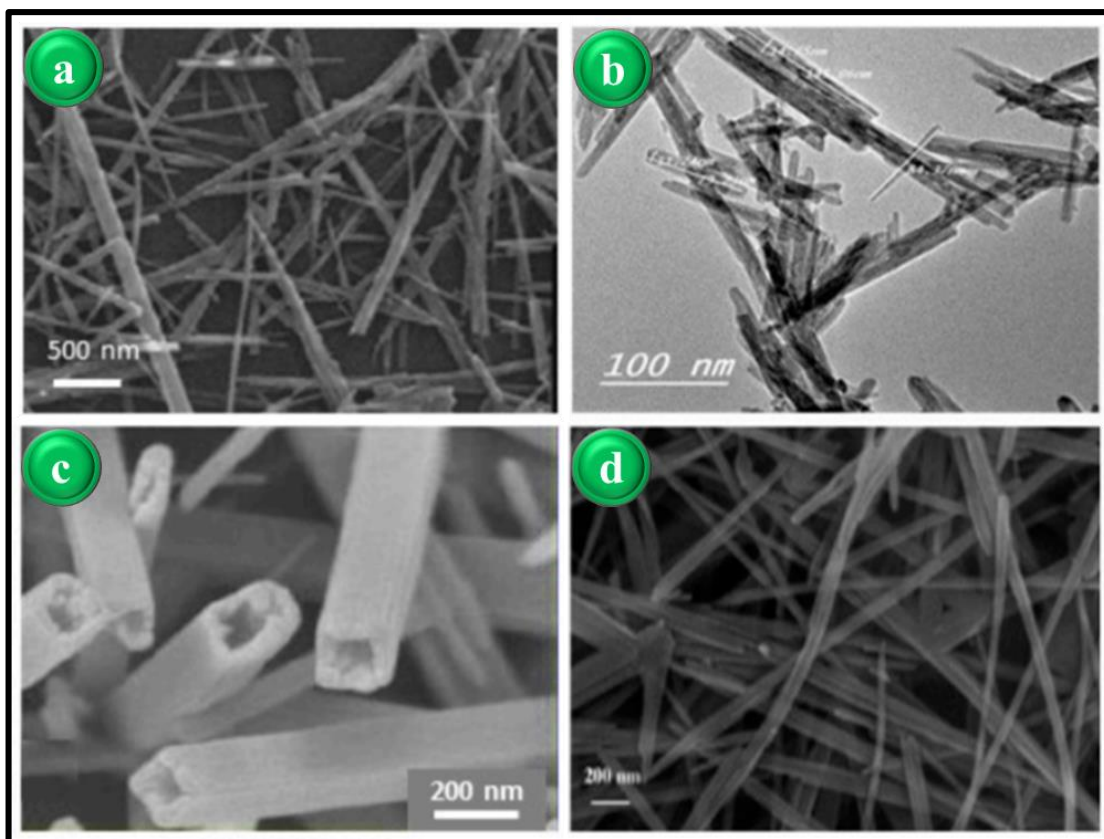


Figure 2.6: Micrographs of MnO_2 ; (a) nanoneedles, (b) nanorods, (c) nanotubes, and (d) nanowires [163, 176].

Furthermore, the surface decoration of CLCNOs by polymers to form CLCNOs-polymer composites through covalent functionalization can also be essential for their technical applications such as in gas sensors [177]. In the case of chemical gas sensors, polymers are also capable of giving high sensitivity, room temperature operation as well as short response time of the sensor but their drawback includes long-term instability and poor selectivity among others [178]. Polymers are classified into two types, namely; conducting (e.g. non-biopolymers, polypyrrole (PPy)) and non-conducting (e.g. biopolymers, polyvinylpyrrolidone (PVP)) [178]. One of the interesting water soluble polymers, is a non-conductive polymer known as polyvinylpyrrolidone (PVP), also called polyvidone or povidone (see **Figure 2.7**).

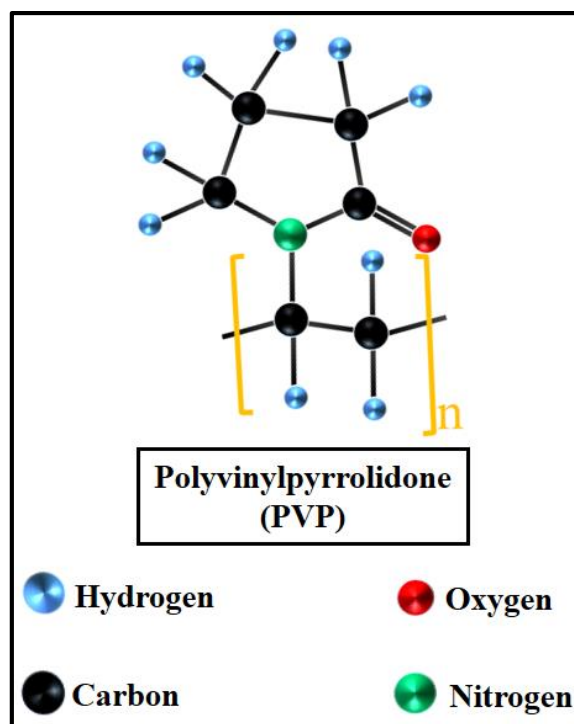


Figure 2.7: Organic chemical structure of PVP [178, 179].

This is a biodegradable, non-toxic and non-ionic amorphous polymer that is variously applied including its application in the food sector due to its high solubility in polar solvents [179, 180]. It is derived from its monomer; N-vinylpyrrolidone [181]. Most importantly, it can be used to disperse nanoparticles and also act as a surface stabilizer [182]. Thus, its physicochemical properties allows for its composite formation which can be formed along with carbonaceous nanoparticles [183]. This kind of a composite can offer positive contribution to gas sensing through the use of carboxylic groups and nitrogen site on the PVP chemical structure [184]. Moreover, the carbon to polymer composite has a high specific surface area and a large number of active sites that will be available to additionally provide reaction sites at which gases can react and be detected [185-187]. This type of a composite can further be enhanced by incorporation of metal oxide nanoparticles to form a carbon-polymer-metal oxide sensitive layer with good electrical properties which can significantly improve the sensitivity of the gas sensor [188, 189].

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CHAPTER 3

Analysis, characterization and measuring or testing techniques that were used in this study

3.1. Introduction

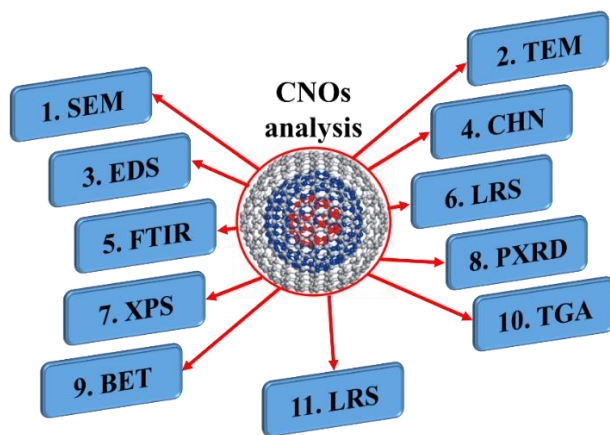
This is the chapter in which the analysis, characterization and measuring or testing techniques that were used in this study are described in details.

Different analytical instruments were used to successfully complete and understand the outcomes following the objectives of the study. The analytical instruments used in this study were mainly for understanding the physiochemical properties of a quasi-spherical nanostructured material in the family of fullerenes, herein named as chain-like carbon nano-onions (CLCNOs) including other nanostructures (e.g. metal nanoparticles (MNs)). Various nanostructured particles (i.e. CLCNOs and MNs) samples were analysed and/or characterised with an aid of different analytical instrumental techniques which offered sets of interpretable analytical data. Moreover, the data sets obtained has allowed for extrinsic and intrinsic properties interpretation of the obtained CLCNOs and/or MNs.

Firstly, the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study the extrinsic and intrinsic structural morphology of nanostructured particles. With the aid of SEM, mainly the carbon nanomaterial samples were further analysed to confirm their cleanliness (i.e. sample elemental composition) using the SEM-coupled energy dispersive X-ray spectroscopy (EDS) analysis technique that makes use of an electron probe which maps the distribution of elements in the sample. Furthermore, the elemental composition of each nanomaterial (i.e. mainly the (doped) carbon samples) can be supported by the data that can be obtained from the carbon, hydrogen and nitrogen (CHN) elemental analyser. Therefore, additional elemental analysis of CNOs was conducted using a carbon, hydrogen and nitrogen (CHN) analyser. Fourier transform infrared spectroscopy (FTIR) was additionally used to analyse the atomic chemical bonding in the structural matrix of the carbon nanoparticles (e.g. the presence of carbonyl and hydroxyl group). Chemical composition analyses were further conducted for all doped carbon nanoparticles samples in which the electronic states and bonding configurations of

doping atoms on carbon framework were investigated by using the X-ray photoelectron spectroscopy (XPS). Following the confirmation of the elemental composition in the structural matrix of the nanoparticles obtained, a laser Raman spectroscopy (LRS/RS) was then used to investigate the structural properties (e.g. amorphous, deformed, disordered, and/or graphitic) of the nanomaterials prepared. In some cases, CLCNOs are regarded as amorphous carbon nanomaterial which can also be classified under poly-crystalline material. Hence, the powder X-ray diffraction (PXRD) analysis technique was employed to confirm and/or study the possible crystallographic phases and structural nature of CLCNOs. This was done in comparison to the results obtained using other analytical techniques such as SEM coupled with EDS and TEM.

Additionally, the PXRD results of other nanostructured metal based samples were also important to understand the type of crystallographic phases metal oxides formed during the synthesis as well as the tentative nanoparticulate sizes obtained. Following the structural nature studies, the surface area studies were done using Brunauer-Emmett-Teller analysis (BET) technique. This was also conducted to investigate the porosity of the material in order to predict the adsorption properties of the nanomaterial produced. After all, mainly the structural architecture/design, chemical strength, thermal stability and/or durability of the carbon nanoparticles samples were investigated. This was achieved using the thermogravimetric analyser (TGA) which allowed for differential thermogravimetric analysis (DTGA). Aimed at investigating the sensing properties of the nanomaterial (i.e. nanocomposites), the Inductance, Capacitance and Resistance (LCR) meter was only used for purposes of resistance related measurements.



Scheme 3.1: Summary of all analysis, characterization and measuring or testing techniques used in the studies conducted.

3.2. Analysis, characterization and measuring or testing techniques used to characterize nanoparticles prepared

3.2.1. Scanning electron microscopy (SEM) analysis

One of the important features of the nanoparticles is its structural shape. The structural shape provides the extrinsic structural details of the nanoparticle. Thus, a scanning electron microscope (SEM) was used to study the structural morphologies of various nanoparticles produced. High resolution micrographs can be obtained using this analytical technique whereby the information about the materials' surfaces can also be obtained.

Basically, this technique make use of a fine beam of electrons that is scanned over a specimen (nanoparticle(s) sample) resulting in the generation of output signals which are emitted by the sample and get identified by the instrument's detector [1]. The micrograph formation follows the allowance of the scanning beam of electrons to excite the nanoparticles contained in the sample and then signals are generated in the two cathode ray tube-type of detectors. Thus, the nanoparticle's micrograph(s) can visualised and recorded following the signals detection [2]. The generated micrograph(s) mainly displaying the; back-scattered electrons, sample current, secondary electrons, and/or transmitted electrons [3]. Moreover, there is a secondary electron micrograph that is usually formed when the back-scattered electrons together with the secondary electrons are detected by the instrument. In this case, the secondary electrons are generated a few nanometres from the surface of the sample. The sensitivity to the structural surfaces of the nanoparticles allows the modern SEM instruments to provide the topological information of the nanoparticles at lower orders of resolutions (i.e. 2 nm) [4]. A stronger interaction of the back-scattered electrons generated within the sample further allows the instrument to provide the required topological information and enables it to give additional information about the sample's composition [5, 6].

In the studies conducted, FEI Nova Nanolab 600 FIB-SEM was used for analysing samples containing nanoparticles in order to study their detailed structural morphology. The instrument was operated at 30 kV using the selected spot size of 0.63 nA. The as-synthesise nanoparticles samples (~ 1 mg) were prepared by placing each amount of the selected sample onto a carbon tape which was mounted on a sample stab. Basically, the preparation of the SEM sample involved placing almost a tip of spatula (~1 mg) of each sample onto the carbon tape and coating the

prepared sample with gold-palladium for about 2 minutes to induce conductivity. The coating process is mostly significant when the samples to be analysed are charging since helps to reduce the level of charges generated during the analysis allowing for flexible analysis.

3.2.2. Transmission electron microscopy (TEM) analysis

Following the details obtained about the extrinsic structural properties of the nanoparticles analysed using SEM. The intrinsic structural properties of the nanoparticles produced were further studied using another microscope based technique. Parameters such as crystallinity, diameter measurements, grain arrangement, particle size phase transitions, and structural morphology of the materials can be determined by using the electron microscopy analysis technique [7]. Thus, TEM is one of the analytical technique that enables the revelation of the finest details of internal structure and the data extrapolations which can also be from a series of reaction products. This technique was firstly demonstrated by Knoll and Ruska in 1931 [8, 9]. It can allow for determination of a step-by-step mechanism of the reaction process [7-9]. High resolution micrographs of samples containing nanoparticles were obtained with an aid of TEM technique. The instrument's micrographs' resolutions can be as high as 2 nm from a high powered beam of electrons that can be accelerated between 120 and 200 kV [10, 11]. The high powered beam of electrons are fundamentally generated from the field emission which is the thermionic source. This electron beam generation is followed by a series of lenses that facilitate their collection and focus the beam of electrons into the optical path. However, the resolution of this type of an electron microscope is controlled by the optical quality of the lenses even though these lenses can be affected by factors such as chromatic and spherical aberration including stigmatism [12].

This type of an instrument has its own operational mechanism which involves micrographing whereby the electrons beam is manipulated using the condenser lenses to focus the beam of electron onto the sample's surface [13, 14]. Thus, the differences during the micrographing process can be introduced by the strength of the diffraction or projector lens [15]. Additionally, part of the beam-surface interactions are transmitted by the produced types of scattering during the sample's analysis [16-18]. This is then succeeded by the focusing the transmitted electrons to the micrograph on the charge-coupled device (CCD) camera using the objective lens [19]. After all, the generated micrograph can be technically enhanced using the objective apertures to change its contrast and it

can be enlarged by down propagation of the transmitted electrons to the column through the intermediate and projector lenses.

In this study, a FEI Technai T12 transmission and/or FEI Technai G2 spirit electron microscope used interchangeably depending on its operational resolution. This instrument(s) were alternatively used to characterise the intrinsic morphological properties and characteristics of nanomaterial(s) produced. The preparation of the sample(s) included a number of steps in which about 1 mg of each sample was put into a glass sample vial containing 5 mL of ethanol. The ethanol solution mixture was then sonicated for 15 minutes in order to disperse the sample in ethanol such that a homogeneous suspension is formed. A drop of the homogeneous suspension was then drop casted and spread on a copper grid (Structure Probe, Inc. (SPI) carbon copper grid (200 mesh)). The copper grid with the sample was allowed to stand and dry at room temperature for 30 minutes. It was then mounted onto an exchange rod of the instrument's sample holder and placed into the instrument's chamber for the sample to be analysed. The diameters and/or sizes of the obtained nanoparticles were measured using a computer based software known as the image-J 1.48v. 100 randomly chosen materials were measured per sample and the diameter or size data was plotted using Origin lab 8.5 software.

3.2.3. Energy dispersive X-ray spectroscopy (EDS) analysis

Coupled with the SEM instrument, the EDS detector allowed for elemental analysis of the prepared samples. The EDS elemental analysis is a technique that involves scanning the X-rays over the samples to determine its elemental composition [20]. The scanned X-rays are mainly generated from the interaction of an electron beam with the selected sample. The generated X-rays have wavelengths and energies that are characteristic of the elements that composed the sample. Hence, the entire process allows for sample's elemental composition and/or distribution to be determined [21]. This technique make use of the X-rays transmitting energy that is directly involved in revealing the elemental composition of the semiconducting sample as the X-rays strike a semiconductor crystal. The electrons in the semiconducting crystal usually absorb a specific amount of energy, putting them into an excited state. This energy is later converted into an electrical signal which is then amplified. Thereafter, the data from the EDS analysis can be presented as the EDX-spectrum, elemental map, histogram, and/or peak patterns [22]. To acquire rapid qualitative and quantitative analysis of an unknown sample, EDS analysis technique can be

used to understand the elemental composition of the unknown sample. Moreover, it can also be used to complement broader analyses data sets such as those from TEM. Hence, in this study EDS analysis technique was used to determine the elemental composition of the nanoparticles produced. The analysis was done through the use of the FEI Nova Nanolab 600 FIB-SEM instrument coupled with the EDS detector in which the samples preparation was similar to those of SEM analysis. Additionally, the Verga3 LMU Tescan SEM coupled with the X-Max 80 EDS detector was used to further identify the elemental composition of the nitrogen containing samples since the EDS detector also allows for identification of light elements including nitrogen.

3.2.4. Carbon, Hydrogen, and Nitrogen (CHN) elemental analysis

The elemental composition of each nanomaterial can be obtained by making use of the carbon, hydrogen and nitrogen (CHN) elemental analyser. The CHN elemental technique has the history dating back to the years when Lavoisier reported on its potential use to accurately determine the elemental composition of organic compounds [23]. The use of this technique allows for precise elemental identification those which mainly compose the sample being analysed. This is a straightforward method for determining whether or not the sample is purely composed of the expected elements which are carbon, hydrogen, and nitrogen specifically [24]. The instrument can be operated unattended since it can be automated as long as the sample weight is best accepted for analysis. Thus, to support the EDS data, further elemental analysis mainly for the doped carbon samples (~200 µg) was achieved using a LECO-932 carbon, hydrogen and nitrogen (CHN) analyser. The instrument used in this study was calibrated with sulfamethazine as a standard for every analysis conducted.

3.2.5. Fourier transform infrared spectroscopy (FTIR) analysis

Distinctively, various nanomaterial usually absorb light in various regions in order to generate the infrared spectrum. Most nanomaterials absorb light in the infrared (IR) region in which various absorptions result in changes in the rotational and vibrational modes of the molecules. One of the useful technique used to identify the kind of absorption in the IR region is the Fourier transform infrared spectroscopy (FTIR). This technique allows for investigating the basic chemical configurations and atomic bonding of different molecules (e.g. organic molecules). Most materials exhibit rotational and vibrational modes of the molecules that depends on the materials' sample

composition which can be due to their dipole moments changing. Consequently, this allows for the absorption frequencies to be determined through use of molecular based vibrational frequencies which also influence the efficiency of the infrared photon energy transfer [25]. Thus, the absorption intensities relies on the measure of the magnitude of the infrared photon energy transfer during the FTIR analysis.

Notably, FTIR is one of the useful technique that can be used for quantification of several chemical components absorbing in the infrared region based on its operation mechanism. The operation mechanism of this instrument can be characterised by the splitting of a beam into two different paths. The wedge of the IR-transparent material can be moved into one of the beams by a material commonly known as potassium bromide (KBr). The intensity of the output beam can be monitored as a function of path difference by using the instrument's detector whenever the beams are allowed to recombine after the desired interference [26].

A Bruker Tensor 27 FTIR analyser was further used to monitor the presence of different functional groups in most of the as-synthesized nanomaterials. The instrument uses the Opus software which allows for various spectra to be obtained and used as unique molecular fingerprints that can be simply distinguished from the absorption patterns of other molecules. This was successfully achieved following the standard background scan per analysis conducted. In each case, a sample was placed on the instrument's analyser and the transmittance scan was performed producing the IR spectrum per sample.

3.2.6. X-ray photoelectron spectroscopy (XPS) analysis

With the importance of understanding the elemental composition of nanomaterial produced. The elemental composition of the nanomaterial can be studied to understand whether the element(s) forming the surface structural matrix of the nanoparticle which mainly includes those that cover the nanoparticles' surfaces. This is accompanied by the information based on the chemical state of an individual element as well as the electronic structure which can provide the density of the electronic states in the nanomaterial. In this case, since XPS follows the photoemission spectroscopy process, it can then be regarded as one of the powerful analytical technique that can be useful to identify the elemental presence on the surface of the nanomaterial [27, 28]. Moreover,

this technique does not only provide the information about the elements existing on the surface of the nanomaterial but it can further reveal the bonding configuration between different and/or similar elements found on the surface of the structural matrix of the nanostructured particle [29]. It makes use of the electron population spectra which are obtained by irradiation of a nanomaterial with a mono-energetic beam of X-rays. The irradiated X-rays results in the emission of photoelectrons from the nanomaterials' surface giving off the measured kinetic energies.

The XPS spectrum can be seen as a plot of the number of electrons which are mainly detected at specific binding energies (chemical shifts) [30]. However, there is a direct relationship between number of detected electrons and the amount of element(s) within the nanomaterial sampling volume. This technique is capable of measuring within the minimum analysing areas from 10 to 200 micrometres taking about 1 to 20 minutes to analyse each sample. Thus, the chemical composition, electronic states and bonding configurations of carbon and nitrogen atoms on the nitrogen doped carbon nanomaterial surfaces produced in this study was determined by XPS. A Physical Electronics Quantum 2000 XPS instrument was used as it uses a monochromatic aluminium (Al) K α source. The instrument was operated at 1486.7 eV and the obtained XPS diffraction peaks were deconvoluted using a Fityk 0.9.8 software.

3.2.7. Laser Raman spectroscopy (LRS) analysis

The nanomaterials' crystallographic and unique vibrational information can be derived from electronic states and phonon energy dispersion in its electrochemical system [31-33]. Thus, the physical properties of the nanoparticles can be easily studied and they can be relevant to electrons and phonons that are in the nanomaterial. The LRS is commonly used to characterise different materials in which it reveals their structural properties. This technique can be used to study the sp² hybridized carbons such as: 3D graphite, 2D graphene, 1D carbon nanotubes and 0D fullerenes [34].

Looking at the structural characterisation of graphitic carbon nanomaterials, the LRS technique offers a valuable information about defects, stacking of the graphene layers and the finite sizes of the crystallites that exhibit parallel and/or perpendicular hexagonal axis. This technique uses an easy, non-destructive, non-contacting and rapid sample measurement process. It is capable of examining the inelastic scattering of light from a sample's surface at ambient conditions (i.e. room temperature and atmospheric pressure). The Raman spectrum of different carbon nanomaterials

are commonly characterised by two dominant spectral features which are the D and D' bands commonly occurring at 1350 cm^{-1} and 1620 cm^{-1} as well as the G and G' bands appearing around 1582 cm^{-1} and 2700 cm^{-1} respectively [35].

A Jobin-Yvon T64000 Ultraviolet (UV) LabRam HR-micro Raman spectrometer with an Olympus BX41 microscope, that makes use of a liquid nitrogen cooled charge coupled device detector working at an excitation wavelength of 514.5 nm at room temperature was used for purposes of analyzing all carbonaceous or carbon containing samples. The laser Raman spectrometer used is fitted with different objective lenses (e.g. 50x objective lens) for imaging purposes. These studies were conducted to determine the effect of varying the parametric conditions of synthesis in terms of graphicity and crystallinity of the products. The Raman data allowed for generation of different spectra which were evaluated and monitored using OPUS 7.1 software. The obtained Raman bands (D- and G-bands) were deconvoluted using a Lorentzian function whereby the peak areas and intensities were measured using the Origin 8.50 software.

3.2.8. Powder X-ray diffraction (PXRD) analysis

Diffraction can occur when light is scattered by a periodic array at specific angles following the constructive interference in a long range order. Thus, this phenomenon can also be seen when the periodically arranged atoms in a crystalline material diffract light. This happens when the wavelength of X-rays are similar to the distance between atoms. This principle is used by the PXRD techniques which helps in terms of the phase identification of components in the nanoparticles. The PXRD technique is usually used to analyse all solid materials both the inorganic and organic solids but amorphous materials such as glass do not produce any significant peak in diffraction pattern since they do not exhibit periodically arranged atoms which are long-range ordered [36]. Since every crystalline material is capable of interacting with the X-rays to produce specific diffraction pattern even if it is in a mixture, PXRD analysis can describe the crystal nature of the sample [37]. This technique allows for measuring the area under the peak of the diffraction pattern which gives a measure of the quantity of that phase present in the sample. The diffraction pattern of a pure substance is like a fingerprint of that substance since this is a non-destructive technique [38]. Hence, the PXRD can distinctively identify and characterise polycrystalline phases whereby the fingerprint of a substance can be derived from the diffraction of X-rays due to the arrangement of atoms. The atomic arrangement might be in a three dimensional order following

repeating sequence making up the crystalline form of the solid nanomaterial. Atoms can be arranged in a regular manner which might bring a describing a solid crystal and eventually the crystallinity of the solid material. Thus, every crystalline structure and the unit cell of the smallest volume of a crystal consists of three axes (i.e. a, b, c) with corresponding angles (i.e. alpha, beta and gamma) respectively [37, 38]. However, some of the solid materials can be regarded as amorphous due to the disordered and/or random arrangement of atoms in their structural architecture.

In this study, a Bruker D2 Phaser XRD that uses Cu-K α irradiation and operated at 30 kV with the X-ray tube at the current of 30 mA over a $10^\circ \leq 2\theta \leq 90^\circ$ scanning range was used. The XRD patterns were collected in Bragg- Brentano geometry with a Lynxeye detector. The scan range of $10^\circ \leq 2\theta \leq 90^\circ$ was used in 0.026° steps, using a standard speed with an equivalent counting time of a second per step. The D2 diffractometer used make use of the Bragg-Brentano geometry with an incident angle defined between the X-ray source and the sample. The diffraction angle (i.e. 2θ) is defined between the detector and the incident beam in which the diffraction vector of the instrument is always normal to the surface of the sample [39]. However, it was important to carefully prepare the sample on the sample zero background holder whereby the glass slide pressing and packing process was applied to obtain a flat and a smooth plane surface with a uniform height in all cases.

All sample scans were acquired over a period of 20 minutes and the data sets were obtained including: lattice parameters, Miller indices and peak patterns. The obtained peaks (from the diffraction patterns) per scan were identified using the inorganic crystal structure database (ICSD). The ICSD generally allows for matching phases which occur at specific 2θ values respectively and the matching process was achieved using a computer evaluation program package known as the EVA (V11.0, rev.0, 2005) software.

3.2.9. Branauer-Emmett-Teller (BET) surface area analysis

Most nanomaterials are sought for their potential applications in different field of studies. Thus, one of the material's important property for better activity is the total surface area of the material. This information can be obtained through the use of BET analysis technique which has important implications for reaction sites that are available on the surfaces of the nanomaterial [40]. This technique enables investigators to determine the specific surface area (SSA) of different materials

since it is the parameter measured on solid materials as the total surface area of a material per unit of mass through the adsorption measurements using the BET isotherms [41]. The SSA is usually measured in m^2/g or m^2/kg since it determines the characteristic property of a material in terms of the material's area per given mass. Alternatively, the SSA can be determined using different measurement methods such as the gas permeability and calculation from the particle size distribution [42]. Unfortunately, these alternative methods are unable to measure much the deep texture of the particles' surface as well as the fine structure of the material's surface.

The BET surface area analysis technic normally uses nitrogen as the gas being adsorbed on the surfaces of powdered solid material(s). In this case, the volumes adsorbed are measured at a constant temperature (e.g. $-195\text{ }^\circ\text{C}$) and relatively at the lowest possible pressure [43]. A non-destructive Micromeritics Tristar 3000 (RS232) surface area and porosity analyser was used to determine the specific surface area of nanomaterials produced. In this manner, the intention was to gather further information about the possible dispersity of the materials. All samples ($\sim 200\text{ mg}$) were degassed under nitrogen gas between $150\text{--}200\text{ }^\circ\text{C}$ for 3 hours followed by analysis measurements which were done at -195°C .

3.2.10. Thermogravimetric analysis (TGA)

It is also important to measure a material's response to being heated and/or cooled such that the relationship between the specific physical properties and decomposition temperature of materials. The basis monitoring of the mass of a material as a function of temperature or time under a controlled temperature and gaseous atmosphere (air and nitrogen) can be achieved using the TGA technique among others (e.g. differential scanning calorimetry (DSC)) [44]. The TGA analysis technique basically involves heating a nanomaterial (i.e. sample) and measuring its weight as it is heated or cooled in the instrument's furnace under controlled atmosphere. The weight loss may be classified as the loss of volatile components (e.g. absorbed moisture) which they are generally seen as low-molecular-mass additives or oligomers [45]. The low-molecular-mass additives usually evaporate between ambient and $300\text{ }^\circ\text{C}$. Moreover, there are volatile degrading products those that are as the result of chain scissions and they generally require temperatures above $200\text{ }^\circ\text{C}$ but not more than $800\text{ }^\circ\text{C}$ [46]. Before the sample analysis, the weighted amount of the sample is loaded in a specialised sample holder (e.g. alumina crucible) which is supported by an instrument's precision balance. The precision balance is responsible for measuring the sample's mass gain or

loss against temperature or time. The completion of the analysis provides an information including that which is about the extent of: catalytic metal residue, decarboxylation, decomposition, oxidation, pyrolysis, solvent water as well as weight percentage ash for various samples depending on the sample's composition [46].

In this study, the TGA technique was applied to characterise the prepared nanomaterials synthesised using different processes. This technique was used to determine the mass of any residue that remained from the as-synthesized nanomaterial. This was done to complement the data from other analytical techniques such as PXRD, Raman and TEM. Moreover, this technique was used to predict the degree of carbon nanoparticles crystallisation as well as defect densities were used to distinguish the prepared carbonaceous material samples as compared to the PXRD and Raman data obtained. Hence, the thermal stability for every nanomaterial prepared for different studies was monitored using a Perkin Elmer Thermogravimetric simultaneous analyser (TGA) conjugated with the Differential Thermogravimetric analyser (DTGA) 6000. About 10 mg of the nanomaterial based sample was put into a high-temperature alumina sample cup or holder that was placed and/or supported on an analytical balance. The analytical balance is located in the instrument's furnace chamber to which the sample can be heated in air (10 °C/min) from 35 °C to 900 °C. During each analysis process, nitrogen is used as the purging gas that flows at 20 mL/min while holding at 35 °C for 5 minutes and also at 900 °C for 5 minutes respectively.

3.2.11. Inductance, Capacitance and Resistance (LCR) meter used for resistance related measurements

Resistance is one of the basic building blocks of passive components which is significantly used in electronic circuits of various electronic devices. Hence, it is a widely used and a very important parameter in the area of passive electrical measurements [47]. This electrical parameter can be measured using a measuring apparatus which is usually a piece of electronic test equipment that has a high class of accuracy known as the Inductance, Capacitance and Resistance (LCR) meter [48]. This instrument is capable of characterising the properties of a particularly material or those of passive components over a wide range of frequencies [49, 50]. It can be operated at specified current, test signals and/or voltage. There are various forms of this type of measuring instruments, such as the hand held and the bench top in which they offer different analysis accuracy, range and

speed [51]. However, the bench top designed LCR meter (i.e. the selected 4284A-Agilent Precision LCR meter) became the equipment of interest based on its ability to be operated at varied frequencies. LCR meter was used with the working frequencies ranging from 20Hz to 1MHz. This equipment was selected considering the fact it has 0.05% basic accuracy with six-digit resolution. The equipment's effective value of varying voltage and/ or current (root mean square (RMS)) which is the equivalent steady direct current (DC, constant) value stands at 20V/40A with 001 steps of the level options. Specifically, the 4284A-Agilent Precision LCR meter is a cost effective solution for precise component (i.e. resistance), semiconductor and material (herein; carbon active composites) measurement. It has a wide range of the testing frequency that allows for testing components of interest to the most commonly used testing standards (e.g. resistance versus time measurements for gas sensors). Hence, this technique meets all the required LCR meter test and measurement requirements since it is equipped with the measurement function key sights including those of conductance (G), capacitance (C), resistance (R), and reactance (X). It has about twenty impedance parameters to access and measure with a constant voltage and current testing signal level.

The common LCR meter general advantages includes; (1) This technique and the process used is more cost effective, environmentally friendly and less time consuming during the testing process/steps, (2) Measurements done with this equipment are more precise offering international standard testing conditions for various components testing, (3) The equipment offers constant voltage and current testing signal level with the impedance parameters to access and measure allowing various test for the component of interest in a device or system. On the other hand, the LCR meter general disadvantages include; (1) Specific operating technologies can impose constraints and/ or limits (e.g. operating at 20V/40A with 001 steps of the level options), (2) The equipment requires special attention by operating personnel among other drawbacks for its use.

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CHAPTER 4

The investigation of phycochemical properties of carbon nano-onions derived from four different oils

4.1. Introduction

Structured carbon nanomaterials (CNMs) have been studied by many researchers due to their unique properties. The carbon allotropes such as fullerenes, nanotubes and graphene are some of the most studied CNMs because of their interesting chemical, electrical, and morphological characteristics [1-3]. This interest in CNMs followed from the discovery of fullerenes in 1985 by Kroto, Heath, O'Brien, Curl and Smalley by vaporization of graphite using a pulse laser was reported [4]. This carbon allotrope is a zero-dimensional (0 D) carbon made mostly of sp^2 bonded carbon atoms (C_n) in a spherical shaped structure [5]. Seven years later, in 1992, Ugarte investigated the curling and graphitization of amorphous carbon by bombarding the amorphous carbon sample with an electron beam [6]. This resulted in the formation of multi-layered fullerenes that were named onion-like graphitic nanoparticles and that exhibited interesting physicochemical properties such as the ability to reversibly accept electrons [7-10]. These nanoparticles are now known as carbon nano-onions (CNOs) following their structural architecture which resembles that of an onion. With the growing interest in the applications of CNOs (e.g. in biosensors, catalysis, energy conversion and storage, hyper-lubricants, and electronics), different methods for the synthesis of CNOs have been explored. These include arc discharge, catalytic chemical vapour deposition (CCVD), ion implantation, thermal annealing and thermolysis (see **Figure 4.1**) [11-20]. While some of these methods produce high quality CNOs, they require sophisticated processes in order to produce CNOs in the gram scale. For example, CCVD requires the use of a catalyst which can be made of different transition metals. The use of metal based catalyst in this method is a challenge whenever a clean (metal free) or high purity product is required and can require an expensive synthesis process due to the cost of the metallic catalyst(s). Moreover, the treatment of the as-synthesized CNOs that often incorporate metal catalyst nanoparticles with concentrated acids (e.g. nitric acid) requires removal of the residual metal catalyst nanoparticles which is a drawback to the method [22]. CNOs can also be made from nanodiamonds but the

thermal annealing of nanodiamonds requires a vacuum set-up operated at temperatures greater than 1000 °C to obtain CNOs in larger amounts [23, 24].

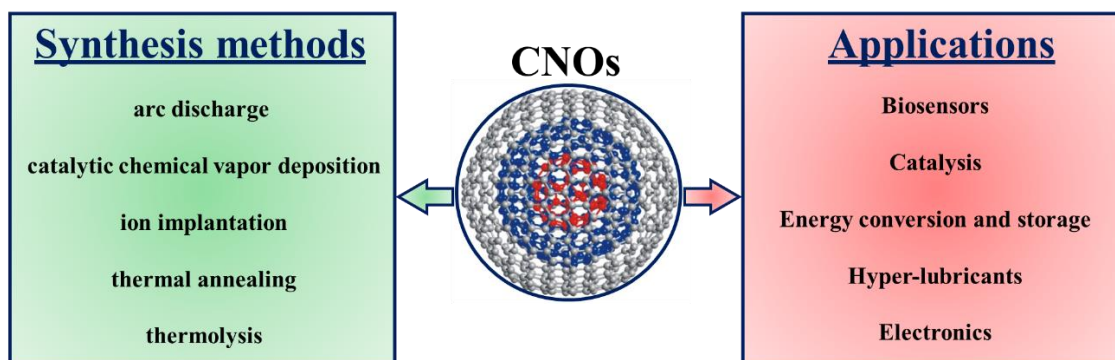


Figure 4.1: Current CNOs applications with various synthesis methods [11-21].

Due to the drawbacks associated with the above methods, researchers have explored the use of various carbon precursors for purposes of synthesizing CNOs with fewer challenges. For example, Ahmed *et al.*, used carrots and tomatoes as natural carbon precursors to generate CNOs [25]. In another study, Mohapatra *et al.*, reported on the use of CNOs made from clarified butter/ghee for application in supercapacitors [26]. In addition, Tripathi *et al.* also reported on essential oil derived CNOs for application in photocatalytic studies [27]. The use of these precursors can be classified as metal catalyst free synthesis processes that are inexpensive, require less intricate procedures and can yield large quantities of CNOs [28]. Thus, their use has an advantage over the other methods (e.g. arc discharge and thermal annealing method) due to reduced contamination by by-products/catalysts and lower production costs. The catalyst free methods that has been developed for the synthesis of CNOs is referred to as the flame synthesis method (FP), and it allows for continuous production of CNOs in air without complexity. This pyrolysis method makes use of liquid fuels (e.g. ghee oil, flaxseed oil and paraffin oil) to give good yields of CNOs in gram scale [26, 27, 29]. CNOs obtained from this method possess structural morphologies with concentric multi-layers resembling that of onion in their spherical shape architecture [30]. Interestingly, this kind of nanomaterial can be functionalized to tailor their structural properties by doping (e.g. nitrogen doping) to alter their electrical properties [31, 32]. It is important to select the appropriate precursor oil when using FP. One of the recent reports showed that different precursor oils, produced materials with different surface properties [33]. More specifically, paraffin oil produced chain-like CNOs (CLCNOs) that had smaller particle sizes as compared to the castor oil produced

CLCNOs with the sizes ranging between 22-32 nm and 44-51 nm respectively. In a separate study, a report was given on the use of grape seed oil and found that the resulting CLCNOs exhibited similar morphology as compared to those reported by Tripathi *et al* [27, 34]. These studies motivated us to look at four long chain hydrocarbon oils; namely; coconut oil, cod liver oil, olive oil and sweet oil as shown in **Figure 4.2**. These essential oils are environmentally friendly and are inexpensive natural plant products [35-44].

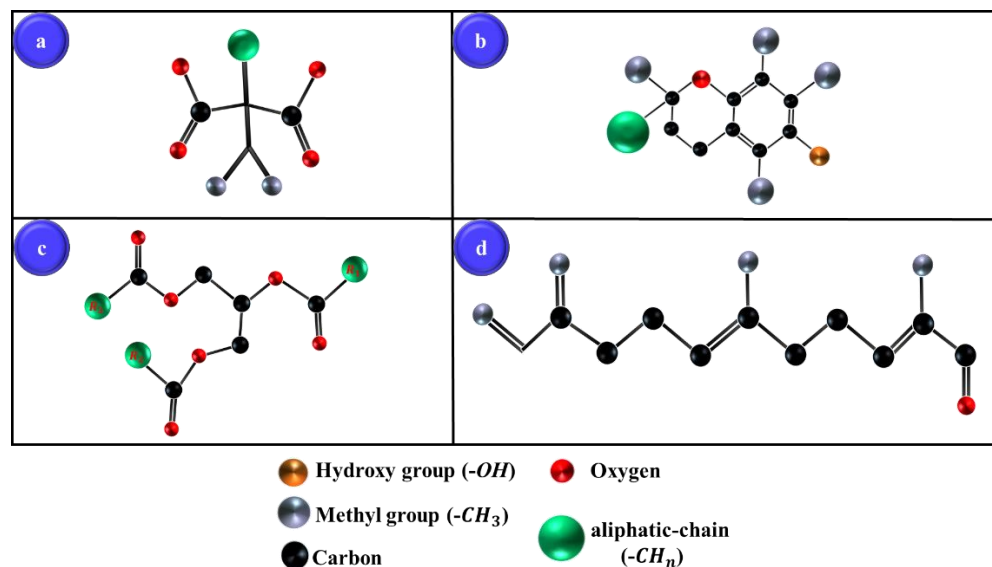


Figure 4.2: The general molecular chemical structure of; (a) coconut oil, (b) cod liver oil, (c) olive oil, and (d) sweet oil.

They are hydrocarbon-rich products mainly composed of fatty acids and some glycerol. They are all edible, providing different human health benefits, and they exhibit similar physicochemical properties which includes combustibility or flammability as well as nearly identical carbon contents (i.e., in the range of 70% to 80%) [45-51]. Hence, they were used for synthesizing CLCNOs using the FP method i.e. oil combustion in air. In this method the CLCNOs (black carbonaceous product) was collected onto different collecting plates (brass, glass) [52]. Thus, a report on how the chemical composition of the oils affects the structural and physicochemical properties of the CLCNOs is given herein. The main aim of this study was to produce high quality CLCNOs for later use in the detection of volatile gases at room temperature.

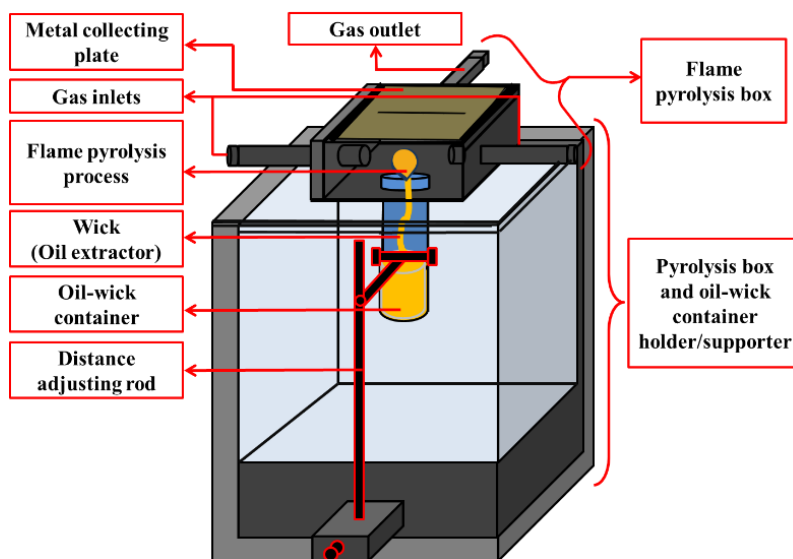
4.2. Experimental

4.2.1. Starting materials

Hydrocarbon oil products (i.e. coconut, cod-liver, olive, and sweet oil) produced by the Hercules Company (Durban, South Africa) and a fibre-glass wick (purchased from a local retailer) were used as received. A polished brass collecting plate (BCP, size: 140×140×1.5 mm) and a steel-tube stand (see **Scheme 4.1**) were made in the University of the Witwatersrand Physical Sciences Workshop. The compressed air was purchased from Afrox (South Africa). Acetone, ethanol, and hexane were purchased from Sigma Aldrich/Merck and were used as received.

4.2.2. Synthesis of CLCNOs using different oils

About 15 mL of each of the hydrocarbon oils was transferred into a 20 mL glass container in which a fibre-glass wick was immersed and allowed to stand in the oil for 30 minutes [53]. The glass container was placed beneath the acetone washed BCP as shown in **Scheme 4.1**, at an optimized distance of ~80 mm between the glass nozzle and the BCP. Finally, the distance between the luminous zone of the flame and the collection plate was maintained at ~20 mm. The wick was ignited to produce a flame at room temperature and atmospheric pressure.



Scheme 4.1: Flame pyrolysis set-up used during the hydrocarbon-oils (i.e. coconut, cod-liver, olive, and sweet oil) flame pyrolysis process.

In a typical experimental process, the as-synthesized product in each precursor oil case was continuously collected onto to BCP plate for 30 minutes. This was followed by collection of the product by scraping the black carbonaceous powder from the BCP using a solid-plastic spatula. The collected CLCNOs were washed with hexane in a Soxhlet extractor to remove excess oil from the carbon nanomaterial sample. The final product was labelled pristine CLCNOs (pCLCNOs). The samples were labelled as p_{coc}CLCNOs, p_{cod}CLCNOs, p_{oli}CLCNOs and p_{swe}CLCNOs for CLCNOs synthesized using coconut oil, cod-liver oil, olive oil, and sweet oil respectively.

4.3. Characterization of CLCNOs

The morphology and characteristics of the CLCNOs produced were studied by scanning electron microscopy (SEM) using an FEI Nova 600 instrument operated at 30 kV. The high magnification images of the CLCNOs were ascertained by transmission electron microscopy (TEM) using a Tecnai G2 30ST operating at 200 kV. This was followed by elemental analysis of all CLCNOs (200 µg) produced in which a LECO-932 carbon, hydrogen, nitrogen and sulphur (CHNS) analyser calibrated with a sulfamethazine as a standard was used. A Bruker Tensor 27 Fourier transform infrared (FTIR) spectrometer was used to further understand the organic functional groups and/or bonding arrangements present in the structural composition of all CLCNOs.

The quality and structural properties of CLCNOs (supported on a silicon wafer (2 mg sample holder)) were investigated using a Jobin-Yvon T64000 Ultraviolet (UV) LabRam HR-micro Raman spectrometer with an Olympus BX41 microscope, that makes use of a liquid nitrogen cooled charge coupled device detector working at an excitation wavelength of 514.5 nm at room temperature. A Bruker D2 Phaser XRD (Cu-K α irradiation and operated at 30 kV with the X-ray tube at the current of 30 mA over a $10^\circ \leq 2\theta \leq 90^\circ$ scanning range) was used to analyse the crystallographic nature of all the samples. The thermal stability of all CLCNOs (i.e. about 10 mg) was determined using a Perkin Elmer 6000 thermogravimetric analyser. Lastly, the Micromeritics Tristar 3000 surface area and porosity analyser was used to determine the surface area and pore volume of the CLCNOs using about 200 mg of each sample.

4.4. Results and discussion

4.4.1. Structural morphology analysis of the CLCNOs

One of the important features for every nanoparticle, is its structural morphology. In this study, the SEM technique was used to obtain the micrographical evidence of the CLCNOs material produced using different precursor oils. Interestingly, the SEM micrographs shown in **Figure 4.3(a-d)** show that all CLCNOs (i.e. p_{coc} CLCNOs, p_{cod} CLCNOs, p_{oli} CLCNOs, and p_{swe} CLCNOs) produced are aggregated and/or conglomerated and are mainly quasi-spherical nanoparticles with particle sizes less than 100 nm.

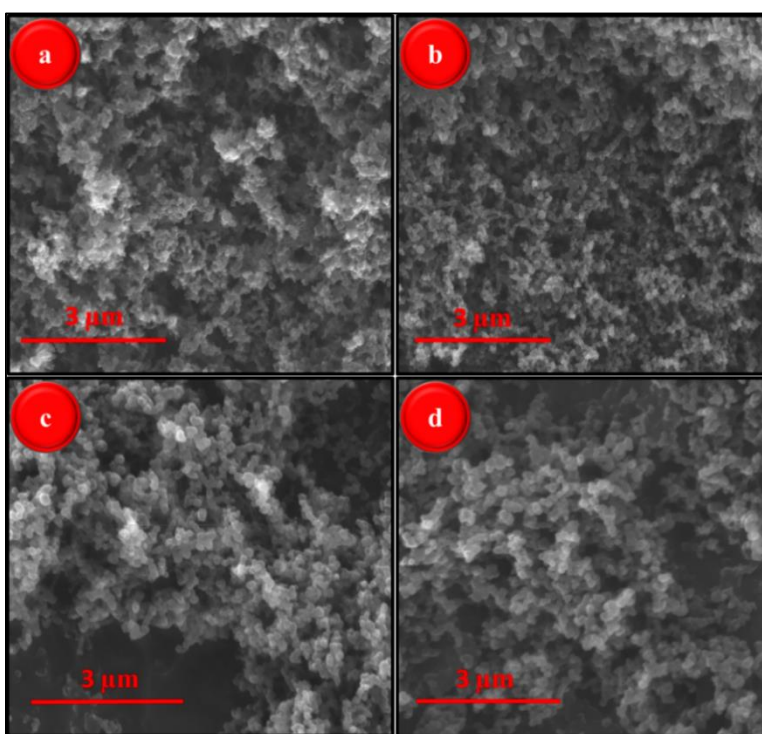


Figure 4.3: SEM micrographs of the produced CLCNOs using different oils; (a) p_{coc} CLCNOs, (b) p_{cod} CLCNOs, (c) p_{oli} CLCNOs, and (d) p_{swe} CLCNOs.

The identified morphological characteristics from the obtained SEM micrographs of all CLCNOs produced are similar to those reported in a previously reported study [52]. Thus, it was observed that the quasi-spherical CLCNOs are always conglomerated irrespective of the organic hydrocarbon oil used to synthesize them through the flame pyrolysis process. The results further suggests that any combustible oil can be used to synthesize a similar nanomaterial. However, the

morphological evidence obtained from SEM results only revealed the external structural details of the CLCNOs nanoparticles.

The TEM technique was used to obtain the internal micrograph evidence of the CLCNOs material produced using different precursor oils. The low magnification TEM micrographs revealed that the as-synthesized CLCNOs exhibited dense or solid quasi-spherical shapes with particle sizes of ca. 63.6 ± 3.7 nm, 68.3 ± 4.2 nm, 54.8 ± 3.3 nm, and 60.7 ± 5.7 nm for p_{coc} CLCNOs, p_{cod} CLCNOs, p_{oli} CLCNOs, and p_{swe} CLCNOs as shown in **Figure 4.4** and **4.5** respectively. Thus, p_{oli} CLCNOs sample exhibited the smallest particle sizes (i.e. 54.8 ± 3.3 nm) as compared to the other samples. This can be ascribed to the reactive poly-aromatic radicals that react to grow different particle sizes depending on the oil chemical properties [54].

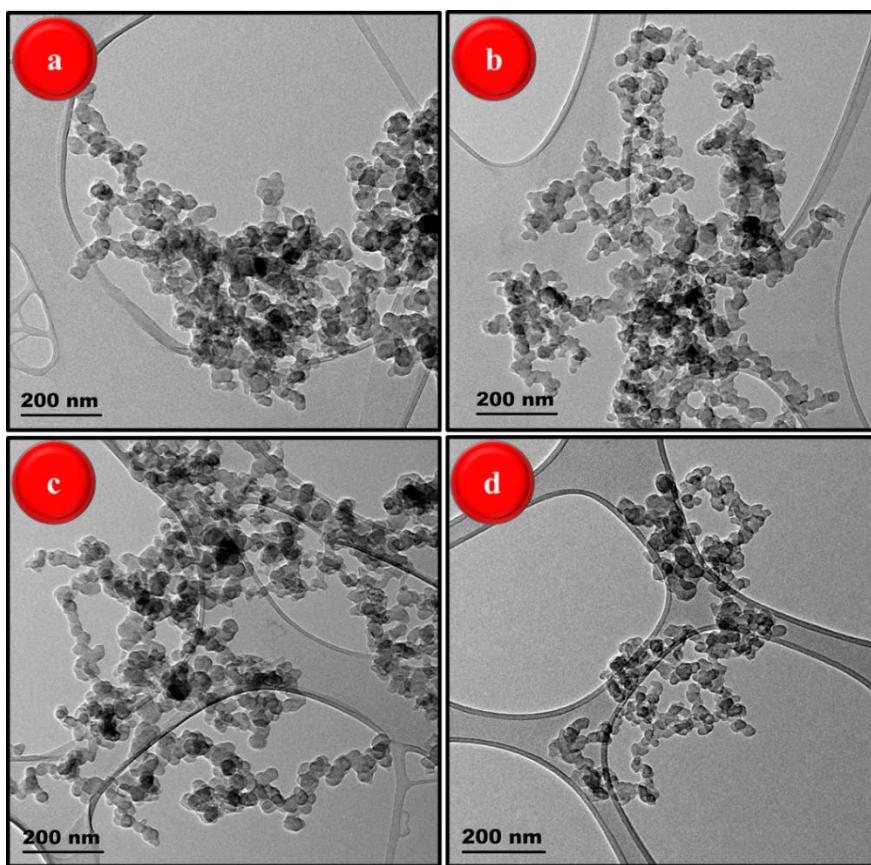


Figure 4.4: Low magnification TEM micrographs of the produced CLCNOs using different oils; (a) p_{coc} CLCNOs, (b) p_{cod} CLCNOs, (c) p_{oli} CLCNOs, and (d) p_{swe} CLCNOs.

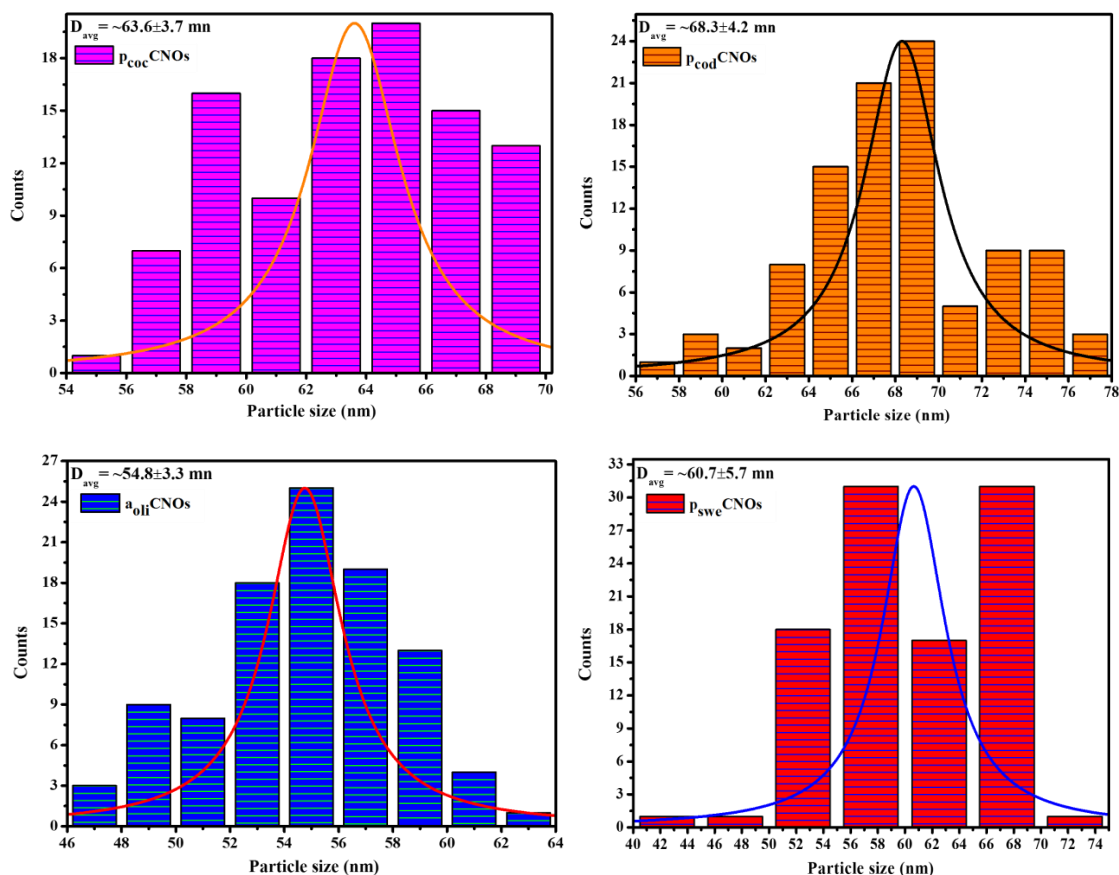


Figure 4.5: Particle size distribution of p_{coc} CLCNOs, p_{cod} CLCNOs, p_{oli} CLCNOs, and p_{swe} CLCNOs obtained using TEM micrographs at low magnification.

The micrographs shown in **Figure 4.6** reveal similar CLCNOs nanoparticles for all samples. The circled regions give examples of areas used to measure the particle sizes. The obtained TEM micrographs showed that for all the samples, the CLCNOs nanoparticles formed conglomerates (see **Figure 4.4** and **4.6**). This observation can be attributed to the Van der Waals forces that promote linkages of quasi-spherical nanoparticles that are comprised of closed cages as shown in **Figure 4.6**. Furthermore, it is also evident that the carbon nanoparticles formed by pyrolysis of different oils are conglomerated in a chain-like arrangement (see **Figure 4.6**). The formed chain-like arranged nanoparticles exhibit multi-layered turbostratic shells.

When the flame pyrolysis process is used to produce CLCNOs using different oils the nanoparticles form as a result of a bottom-up synthesis approach in which the hydrocarbon molecules break down due to the heat produced by the flame [55]. Basically, when the oil burns it produces a dark zone whereby the pyrolysis of the fuel (i.e. hydrocarbon oil) usually begins due to an inadequate oxygen supply. The inadequate oxygen supply promotes combustion of the

hydrocarbon oil to form various carbon containing species that eventually react with one another to form carbon nanoparticles. Furthermore, these carbon nanoparticles can also be formed in the luminous zone (orange-yellow region of the flame) [56]. Moreover, when using this type of the synthesis method to produce CLCNOs, the nanoparticles can exhibit various organic functional groups (e.g. carboxylic groups) depending on the precursor oil used as discussed in previous reports [52, 57].

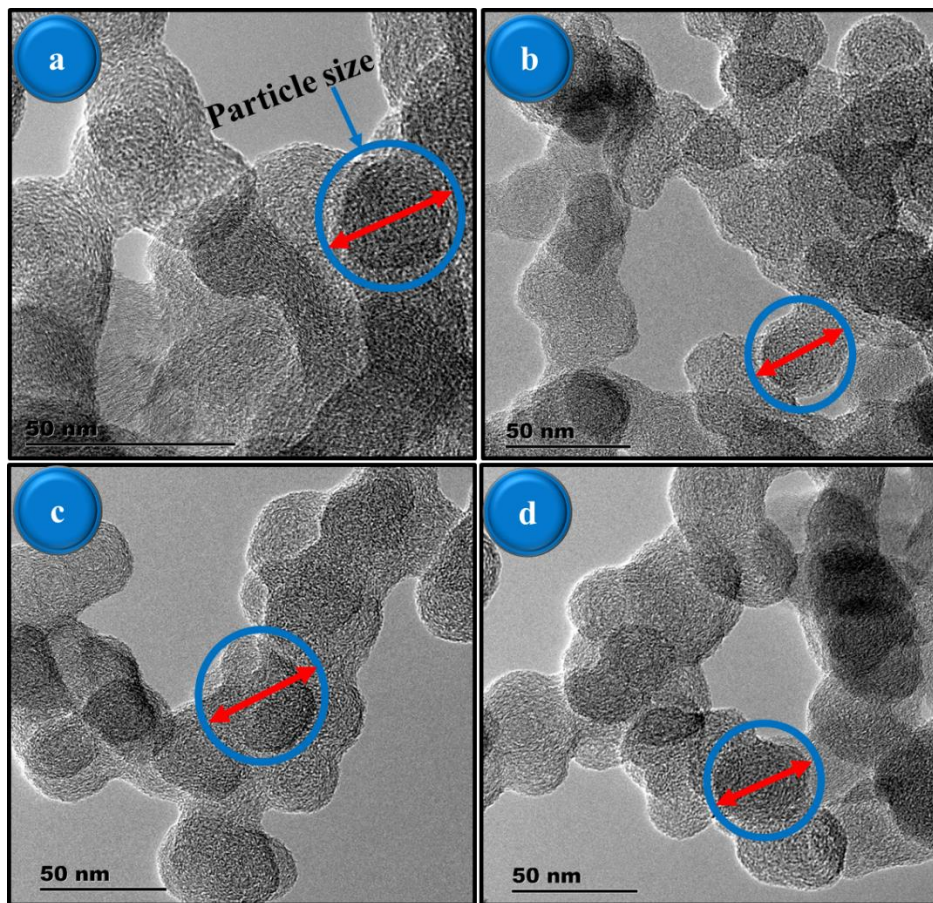


Figure 4.6: High magnification TEM micrographs of the produced CLCNOs using different oils; (a) p_{coc} CLCNOs, (b) p_{cod} CLCNOs, (c) p_{oli} CLCNOs, and (d) p_{swe} CLCNOs.

The structural morphology of chain-like CLCNOs is independent of the precursor oil. The results in **Figure 4.7(a)** and **(b)** further reveals that the nanoparticles (<100 nm) formed using olive oil are accreted resembling a chain (also see the arrow in **Figure 4.7(b)**). The TEM micrograph in **Figure 4.7(c)** also reveals that there exist concentric turbostratic shells forming CLCNOs nanoparticles. Additionally, the p_{oli} CLCNOs nanoparticles also exhibit short-range ordered

multiple concentric layers with the lattice fringe spacing of ca. 0.35 nm (see arrows in **Figure 4.7(c)**). Hence, the obtained lattice fringe spacing also confirms the presence of disordered graphitic carbon shells (i.e. turbostratic shells) [58-60]. However, it was not easy to determine the number of shells contained by all the as-synthesized CLCNOs as reported by Zheng and Zhu due to the presence of short-ranged multi-layers [61].

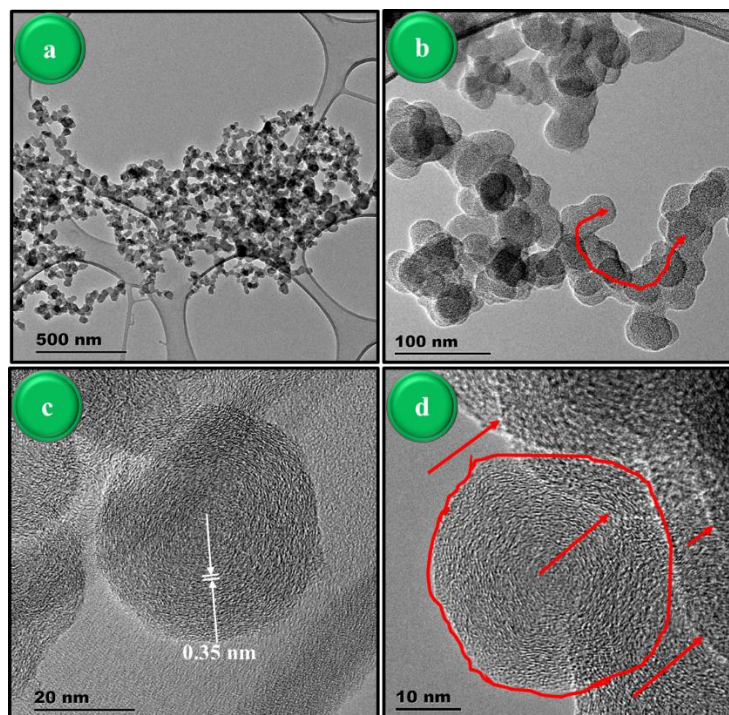
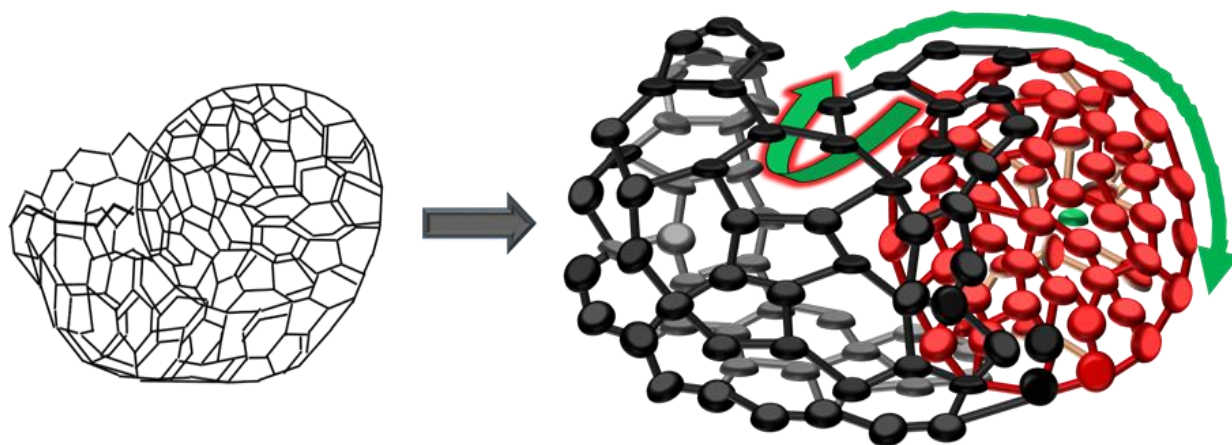


Figure 4.7: High magnification TEM micrographs of the selected CLCNOs produced using olive oil (p_{oli}CLCNOs); (a) smaller nanoparticle sizes, (b) chain-like connection (i.e. conglomeration) of CLCNOs nanoparticles, (c) inter-layer spacing of the multi-shells, (d) quasi-spherical shape of CLCNOs nanoparticle and CLCNOs multi-stacking regions.

The formation of the short-ranged multi-layers can be attributed to the types of radicals that facilitate the growth process of individual particles during the FP process. Typically, the FP process is similar to the cracking process of macromolecules. In this process, the oil macromolecules break down into constituent micro-molecules and this mainly takes place in the luminous zone of the diffusing flame. When the constituent micro-molecules are formed they further break down to release chemically reactive carbon and hydrogen radicals [62].

The luminous zone of the flame (at $\sim 1000\text{ }^{\circ}\text{C}$) is regarded as a diffusing flame since the air and oil react through diffusion before the oil burns and breaks down into constituent micro-molecules and/or radicals [63]. Consequently, different constituent micro-molecules and/or radicals nucleate and aggregate into aromatic carbon rings. The different molecular shapes, sizes and stable intermediates formed with relatively strong sp^2 hybridised carbon covalent bonds are afforded by the aromatic rings [64].

The aromatic carbon rings grow in size by condensation of more carbon fragments in a rapid reaction until the formation of polycyclic aromatic hydrocarbons (PAHs) is achieved. These PAHs accrete to form carbon lattices and ultimately the quasi-spherical carbon nanoparticles (QSCNPs) usually seen as a black carbonaceous powder (see **Scheme 4.2**). The QSCNPs formed by this process usually consist of short-range concentric multi-layers of fullerene-like carbon structures [65]. Eventually, QSCNPs connect in a chain-like arrangement and conglomerate to form larger carbonaceous particles. The later formed nanoparticles follow a “*snowfall-like*” accretion process to give the chain-like carbon nano-onions with cross sectional appearance and structural architecture resembling that of an onion, as discussed in the work reported previously [52, 66, 67]. Other radicals formed during the pyrolysis process can also react with oxygen in the air to produce carbon dioxide (CO_2) and water (H_2O) [65, 68]. The arrows shown in **Scheme 4.2** show the stacking process used to form the quasi-spherical CLCNOs with layers on top of one another to give the CLCNOs agglomerates.



Scheme 4.2: Curling “*snowfall-like*” accreting process that forms multi-shelled CLCNOs.

4.4.2 Elemental analysis and functional groups identification in the CLCNOs structural matrix

In this study the CHN elemental analysis technique was used to study the elemental composition of the synthesized materials. **Table 4.1** reveals that all samples are predominantly made of carbon and hydrogen atoms. All samples contained about 85% of carbon atoms. Moreover, these samples exhibited more than 5% but less than 10% of hydrogen atoms in their structural matrix. This confirms that they can all be classified as a hydrocarbon based nanomaterial. Considering a 100% elemental composition for each sample, there exist other elements than carbon and/or hydrogen and this is typically ascribed to oxygen atoms as shown in **Table 4.1**.

Table 4.1: CHN data of CLCNOs synthesized using flame pyrolysis.

Sample	Element		
	C (%)	H (%)	O (%)
p_{coc}CLCNOs	91.32	6.87	1.81
p_{cod}CLCNOs	91.84	6.93	1.22
p_{oli}CLCNOs	90.42	7.54	2.04
p_{swe}CLCNOs	90.19	7.92	1.89

Since the synthesis process was carried out in air, the oxygen groups in the structural matrix of all CLCNOs nanoparticles are present after reaction with the ‘unsaturated’ carbon atoms binding with the oxygen to make a stable structure. Thus, different functional groups containing oxygen are found in the CLCNOs with their amount dependent of the precursor oil that was used in the pyrolysis process. Since the elemental compositions of the oils are similar they exhibit indistinguishable chemical properties. The presence of different functional groups in the as-synthesized CLCNOs was detected using the FTIR technique. The FTIR spectra of the four CLCNOs samples analysed are presented in **Figure 4.8**. The spectra shown in **Figure 4.8(a)** indicates that, for all samples (i.e. for p_{coc}CLCNOs, p_{cod}CLCNOs, p_{oli}CLCNOs, and p_{swe}CLCNOs) there exist several peaks of interest. The peak positions and functional group(s) assignments of all CLCNOs synthesized are summarized in **Table 4.2**.

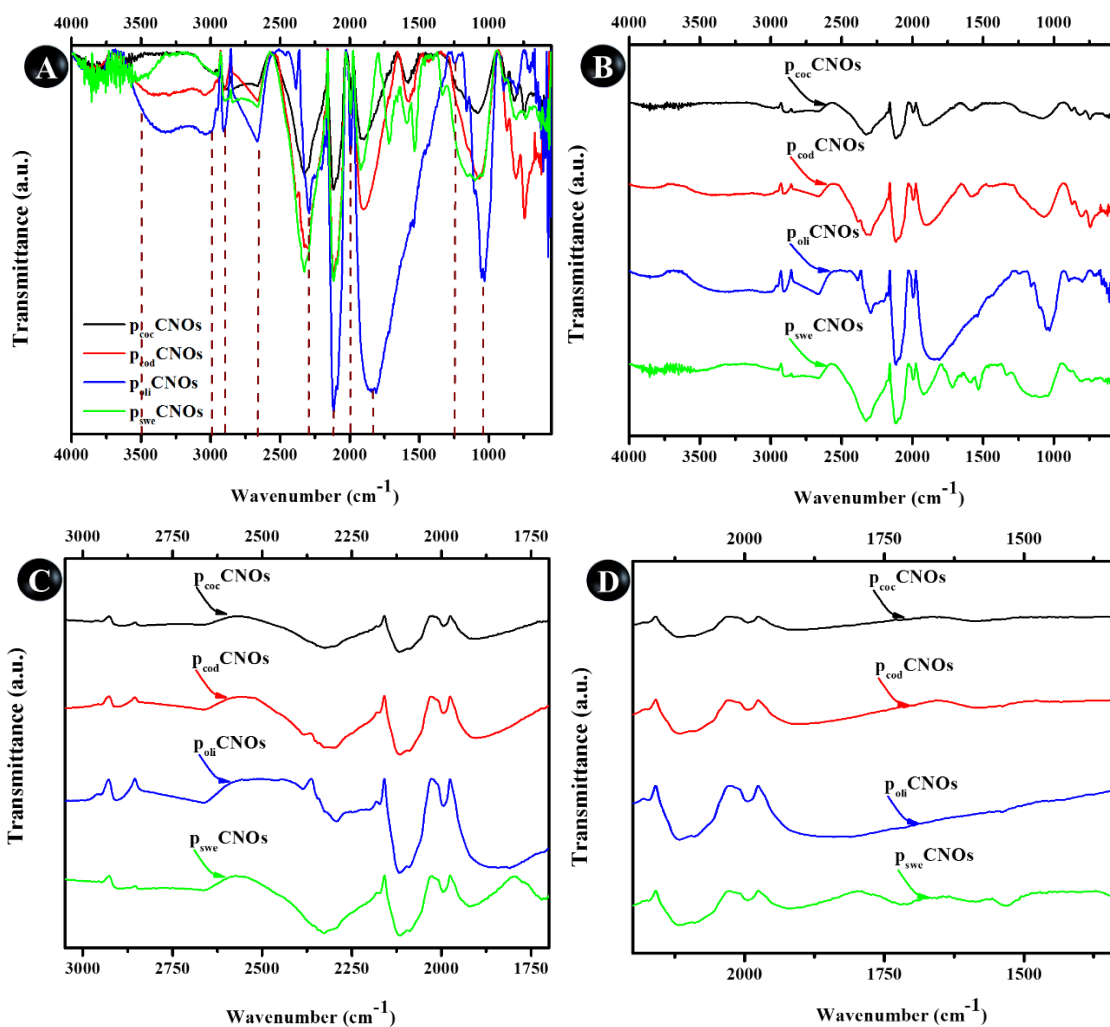


Figure 4.8: FTIR spectra of p_{coc}CLCNs, p_{cod}CLCNs, p_{oli}CLCNs, and p_{swe}CLCNs; (a) all functional groups peaks, (b) peaks for O-H and C-H groups, (c) peaks for CO₂ and C-C groups, and (d) broad peak for C=O and O-C-O groups.

Table 4.2: FTIR data of all CLCNOs synthesized using different oils.

Functional Group (possible assignment)	Peak position (wavenumber (cm ⁻¹))			
	p _{coc} CLCN	p _{cod} CLCNOs	p _{oli} CLCNOs	p _{swe} CLCN
	Os			Os
$\nu(\text{O-H})$				3447-3300
$\nu(\text{=C-H})$				3200-3010
$\nu_{\text{as/s}}(\text{C-H})$				2910
$\nu(\text{C-H})$				2660
CO_2				2396
$\nu(\text{C-C})$				2266-2120
$\nu(>\text{C}=\text{C}=\text{C}<)$				1811
$\nu(\text{C=O})$				1795-1720
O-H				1620
$\nu(\text{C=C})$				1610-1545
$\nu(\text{C=C})$				1415-1410
C-O				1277
$\delta(\text{=C-C=})$				1226
$\nu(\text{=C-C=})$				1142
$\nu(\text{C-O})$				1028
$\delta(\text{=C-C=})$				983
$\nu(\text{C-O})$				879
$\delta(\text{C-C})$				786
(C-C)				710

δ : Bending or deformation vibration type, ν : Stretching vibration type, $\nu_{\text{as/s}}$: asymmetrical or symmetrical stretching vibration type.

A broad peak between 3447 and 3300 cm⁻¹ is usually associated with hydroxyl group (O-H) stretching modes [69, 70]. The broad O-H peak that occurs between 3500 and 3000 cm⁻¹ can be attributed to the presence of hydroxyl groups that are from adsorbed water molecules, intermolecular hydrogen bonded O-H:O-H, or surface carboxylic and phenolic groups (see **Figure 4.8(a)** and **(b)**) [71, 72]. The spectra in **Figure 4.8(c)** show that all CLCNOs samples exhibit C-H

asymmetric and symmetric stretching vibration modes ($2990\text{--}2900\text{ cm}^{-1}$) and C-C stretching vibration modes between $2266\text{--}2120$ (see **Table 4.2**) [73, 74]. These results confirm that all samples are mainly made of carbonaceous material [75].

The sharp peak at around 2396 cm^{-1} for all the samples as shown in **Figure 4.8(a)** and **(c)** can be ascribed to the presence of carbon dioxide (CO_2) molecules [76]. The presence of carboxyl groups (e.g. C=O) in the structural matrix of all CLCNOs can be confirmed by the broad peak between 1795 and 1720 cm^{-1} as shown in **Figure 4.8(d)**. This type of functional groups can be assigned to the presence of aromatic rings bonded to carboxylic acid groups formed by oxidation of hydroxyl groups that are associated with C-C bond cleavage [75-77]. The samples also exhibited other functional groups such as =C-C= and C-C with their respective peaks appearing around 1226 , 983 and 786 cm^{-1} that are due to bending or deformation type vibration modes respectively [78, 79].

Additionally peaks around 1277 cm^{-1} also indicated the presence of carboxylic groups in the structural matrix of CLCNOs [80]. Thus, the spectra for all materials analysed were similar, which signifies that the CLCNOs produced by the pyrolysis method had a common structural matrix. However, it can be suggested that the chemical properties are the same due to the use of oils that exhibit different molecular structures that are broken down into macromolecules, micromolecules and PAHs radicals during pyrolysis (see **Figure 4.1**).

4.4.3. Raman spectral characterization of CLCNOs

The Raman spectrum of carbon nanomaterials commonly presents two prominent peaks commonly known as the D-band and G-band [81, 82]. As expected, all the Raman spectra for CLCNOs synthesized samples displayed two prominent “*finger-print*” peaks, corresponding to the D-band in the region 1337 and 1346 cm^{-1} as well as the G-band between 1583 and 1595 cm^{-1} (**Figure 4.9(a)**). Following the analysis, all samples presented D-bands that were positioned in the expected Raman shift region. The appearance of the D-band can be ascribed to the disorder induced by C–C vibrations corresponding to the disruptions of the sp^2 hybridized carbon bonds. It can be suggested that the disruptions are due to the presence of dangling bonds, sp^3 bonding, C and H adatoms, intercalated C and H atoms, vacancies, as well as other carbon rings arising from structural conformations depending on each sample analysed respectively [83, 84]. In the case of quasi-spherical nanoparticles, the breathing mode of the six-fold aromatic rings in their structural

matrix can also be indicated by the appearance of the D-band in the corresponding “*finger-print*” region [82, 83, 85].

All CLCNOs samples also exhibited the presence of a G-band which is mainly ascribed to the in-plane vibration modes of the sp^2 carbon bonds [86, 87]. It is also important to note that the breadth of both bands (i.e. D- and G-band) and their intensity and position can be useful measurement for determining the quality of CLCNOs. Moreover, the defects and/or disorder density ratio (I_D/I_G) is directly related to the extent of disorder in the form of sp^3 hybridized carbons and the presence of either longer or shorter graphitic fragments [88, 89]. Hence, to quantify the degree of graphitization of all as-synthesized CLCNOs, the ratio of the D-band area to that of the G-band area (I_D/I_G) (fitted with Voigt line shapes using the Origin 8.5 inbuilt fitting fixture, see **Figure 4.10**) was estimated for all CLCNOs samples. It is evident that the I_D/I_G values of all CLCNOs produced were $ca. > 1$, which indicates some graphitization in the structural matrix of the samples as shown in **Figure 4.9(b)** and **Table 4.3**.

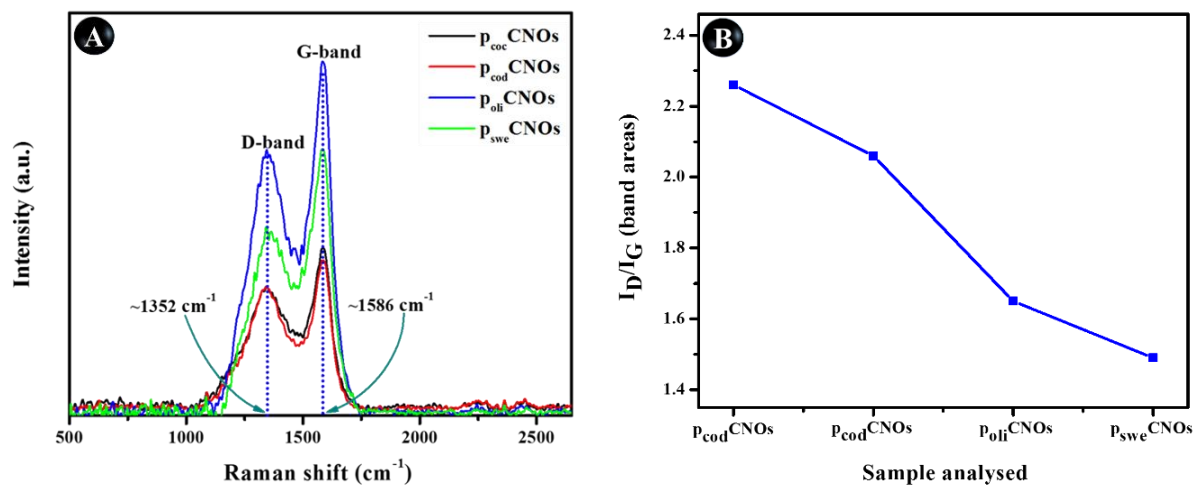


Figure 4.9: (a) Raman spectra of all CLCNOs, (b) the I_D/I_G plot obtained using the D- and G-band areas for each sample.

The summarized data in **Table 4.3** reveals that for all the samples, the D- and the G-band are positioned at different Raman positions. The comparable shifts signifies the curvature distortion since the curved carbon nanostructures such as carbon spheres as well as CLCNOs, usually exhibit both the armchair and zig-zag edges at the graphitic boundaries [81, 90, 91]. The peak shifts can also be attributed to the number of edges and/or in-plane terminations of either a pentagonal or

hexagonal carbon network of the CLCNOs outer shells which can in turn change the sp^3 to sp^2 carbon fraction.

The spectra in **Figure 4.9(a)**, also show that the quantity of sp^2 to sp^3 carbon content is higher for all samples as the G-bands are more intense than the D-bands. For all samples, the D- and G-band full width at half maximum (FWHM) were higher than ca. 190 and 80 respectively as shown in **Table 4.3**.

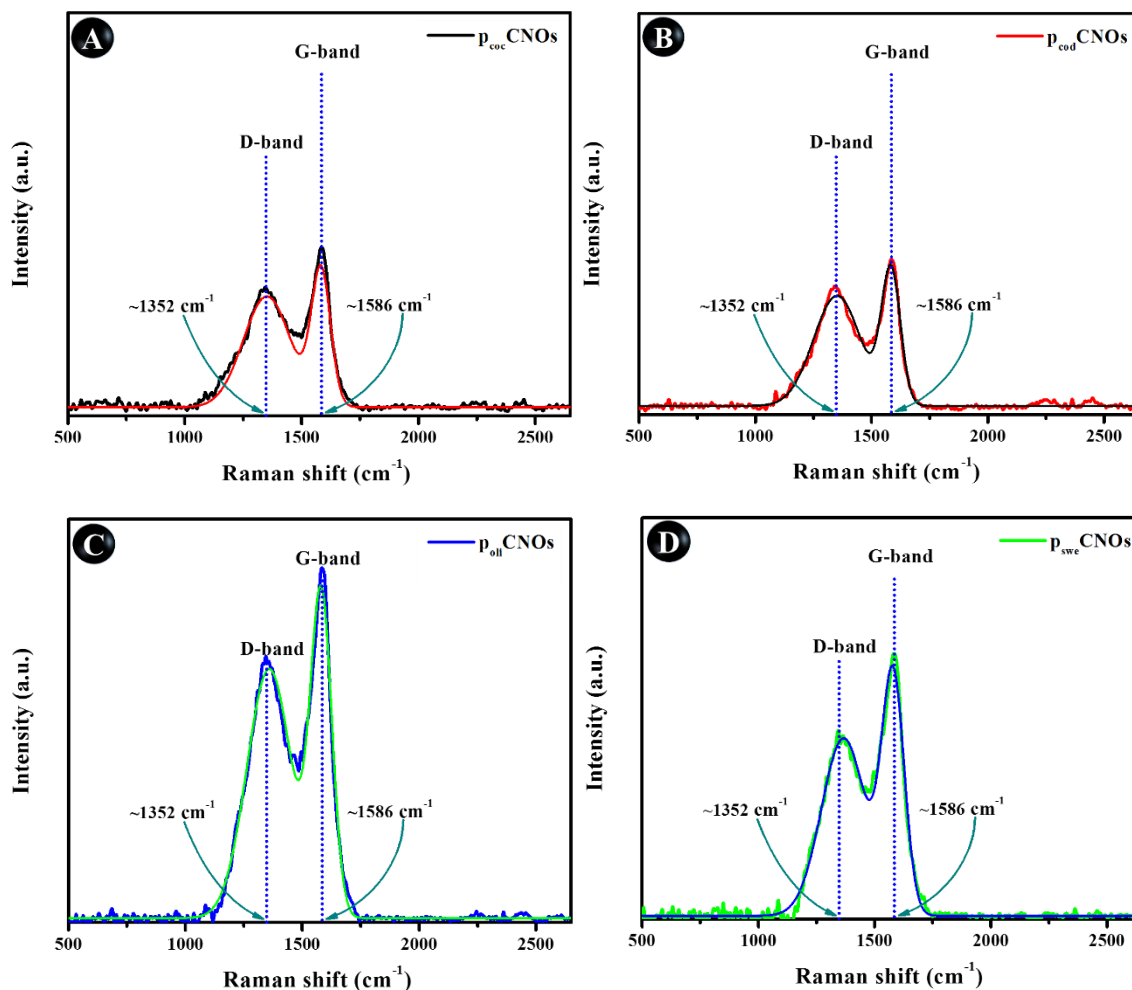


Figure 4.10: Deconvoluted Raman spectrum of; (a) p_{coc} CLCNOs, (b) p_{cod} CLCNOs, (c) p_{oli} CLCNOs, and (d) p_{coc} CLCNOs synthesized using different oils.

When comparing the FWHM results, p_{coc} CLCNOs presented a higher FWHM (ca. 227.6) than the other samples and this is ascribed to the increased amount of structural disorder. It can also be attributed to the exposure of the in-plane terminations of either pentagonal or hexagonal carbon

network of the p_{coc} CLCNOs outer shells as well as the presence of more amorphous carbon impurities as indicated by the higher I_D/I_G ratio. Thus, it is noted that the exposure of the in-plane terminations on the CLCNOs shells can be proposed to contribute to the amount of zig-zag edge defects, thereby increasing the sp^3 content within the curvatures of the CLCNOs [92-94].

The defects and/or disorder density ratio (I_D/I_G) for all doped samples were estimated and the results showed that the ratios were ca. 2.26, 2.06, 1.65, and 1.49 for p_{coc} CLCNOs, p_{cod} CLCNOs, p_{oli} CLCNOs, and p_{swe} CLCNOs respectively (see **Table 4.3**). This revealed a decreasing I_D/I_G trend suggesting the remarkable and variable sp^3 hybridized carbon content that contributes to the presence of defective outer shell edges in the structural matrix of different CLCNOs. Moreover, this observation can be ascribed to the presence of surface functional groups that depend on the molecular structure of the precursors as shown by the peak appearances in the FTIR spectra.

Table 4.3: Raman data of all CLCNOs synthesized using different oils.

Sample	Raman shift (cm^{-1})	Raman shift (cm^{-1})	I_D/I_G	FWHM	FWHM
	D-band	G-band		D-band	G-band
p_{coc} CLCNOs	1357.3	1584.3	2.26	227.6	80.9
p_{cod} CLCNOs	1351.6	1583.3	2.06	202.8	81.7
p_{oli} CLCNOs	1358.7	1581.6	1.65	191.2	91.5
p_{swe} CLCNOs	1366.8	1579.6	1.49	190.7	96.9

I_D : area of the D-band, I_G : area of the G-band, I_D/I_G : ratio of the areas (i.e. for D-band and G-band respectively).

4.4.4. Crystallographic phase, surface area and porosity of the CLCNOs

The distinctive identification and characterization of polycrystalline phases exhibited by the as-synthesized CLCNOs were determined by using the PXRD technique. By using this technique, investigations on the atomic arrangements derived from the diffraction of X-rays were carried out in order to understand the crystallinity and/or polycrystallinity of all the CLCNOs. The diffractograms in **Figure 4.11(a)** revealed that different CLCNOs were mainly composed of polycrystalline carbon atom arrangements without any other impurities (e.g. metals). All CLCNOs patterns showed carbon peaks centred at $2\theta = 25.0^\circ$ and 43.5° corresponding to the (002) and (004) planes of carbon. These patterns confirmed the polycrystalline nature of the carbon nanomaterials while the appearance of peak centred at $2\theta = 43.5^\circ$ signified that the CLCNOs produced contained

graphitic carbon domains [95]. Interestingly, **Figure 4.11(b)** showed FWHMs with values that are less than 5 and 3 in the case of the 002 and 004 peaks observed for all samples respectively. It was also noted that the highest FWHM for the 002 and 004 peak was obtained from p_{cod}CLCNOs (ca. 4.6 (002) and 2.6 (004)). This is also an indication of a poor multi-layering arrangement of the p_{cod}CLCNOs as compared to the other samples. However, the data in **Figure 4.11(b)** also support the observations made in the TEM micrographs of short range ordered layers. Hence, the Raman spectra suggested the presence of structural distortions or disorders that exist in polycrystalline carbon nanoparticles.

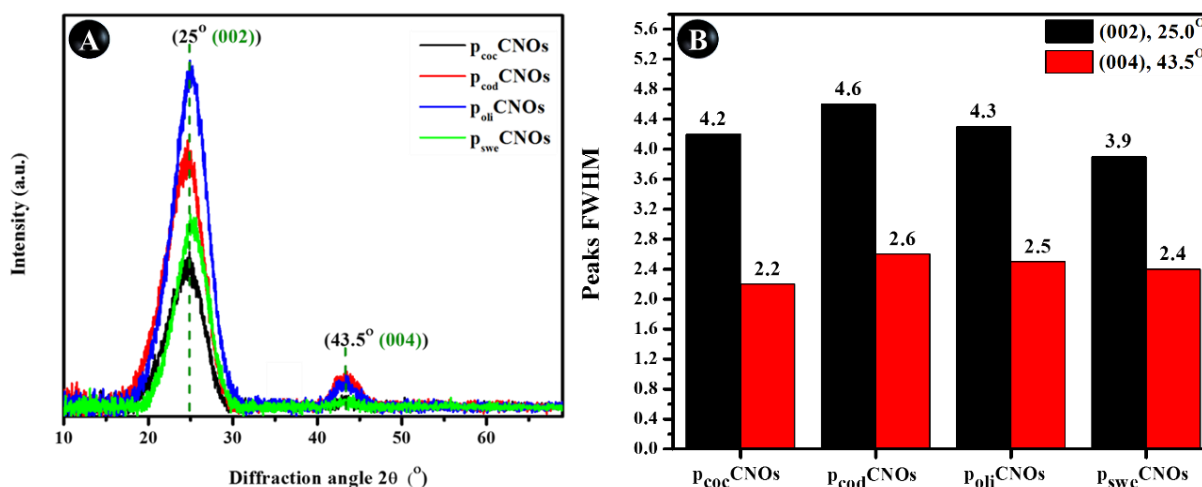


Figure 4.11: (a) X-ray diffractograms, (b) peak breadth (i.e. FWHM) histogram for all CLCNOs.

The BET surface characterization technique revealed that the surface areas of the samples were greater than 50 m²/g but less than 70 m²/g. The p_{oli}CLCNOs (ca. 68.8 m²/g) had the highest surface area when compared to the other samples (see **Figure 4.12**). This can be due to the increased content of adatoms and/or other functional elements on the surface of p_{oli}CLCNOs nanoparticles as suggested by the CHN results. The plot of the pore sizes in **Figure 4.12** showed that all CLCNOs samples exhibit inter- and intra-particle pores. Hence, the defect densities obtained from Raman spectra could be largely contributed by these inter- and intra-particle pores. The pore sizes are different for all CLCNOs samples which can be due to the possible formation of intra-particle pores on the outer shells of CLCNOs depending on the structural conformation of the CNO nanoparticles. It was also observed that p_{oli}CLCNOs exhibited larger pore sizes as compared to the other samples (see **Figure 4.12**).

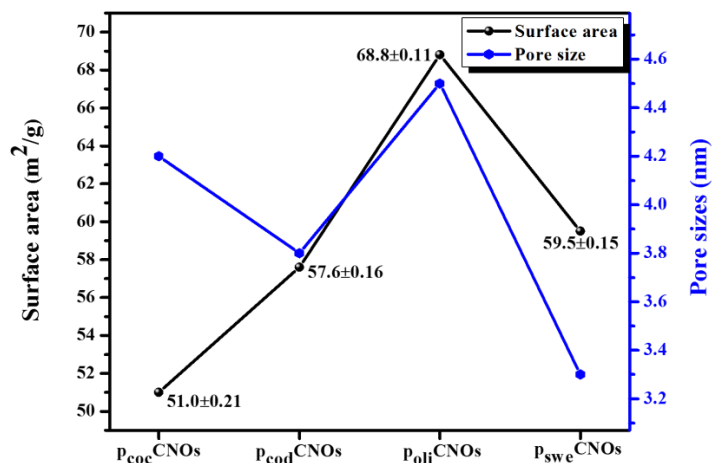


Figure 4.12: Plot representing the pore size and surface area of different CLCNOs.

Thus, the BET results indicate that the surface properties of all CLCNOs (i.e. the surface area and pore size) are influenced by the oil used during the synthesis process which could affect the adatoms attachments, curvature and direct contact area of the carbon nanoparticles.

4.4.5. Thermal stability of as-synthesized CLCNOs

The TGA results shown in **Figure 13(a)** provides an indication of the impurity levels (residual mass) after the completion of decomposition for the CLCNOs. Additionally, the obtained TGA profiles show varying slopes of all the profiles obtained which suggest varying degradation of multi-layered CLCNOs [96]. All samples have only small amounts of amorphous carbonaceous as the on-set decomposition temperatures (ODTs) were less than 450 °C (see **Figure 14(a)**). Notably, the p_{oil}CLCNOs sample presented a higher ODT as compared to the other CLCNOs (**Figure 14(a)**) as shown by values of 552 °C, 532 °C, 573 °C and 554 °C for the p_{coc}CLCNOs, p_{cod}CLCNOs, p_{oli}CLCNOs, and p_{swe}CLCNOs respectively. In addition, the first-order derivative weight loss (FDW) curves for all samples are shown in **Figure 13(b)**. The observed FDW curves for p_{coc}CLCNOs, p_{cod}CLCNOs, p_{oli}CLCNOs, and p_{swe}CLCNOs were fitted with Voigt line shapes using the Origin 8.5 inbuilt fitting fixture. The data showed broad fitted peaks with the calculated FWHM of ca. 127.7, 128.1, 156.4 and 137.3 respectively. The p_{oli}CLCNOs exhibited a broader shape of the FWD curve (i.e. ca. 156.4) as compared to other samples (see arrow in **Figure 14(b)**).

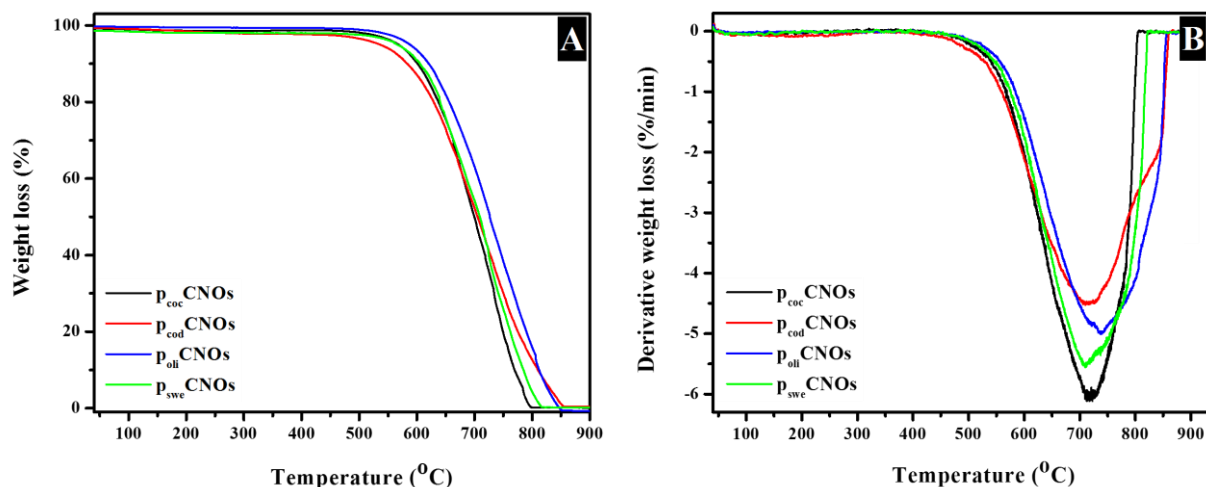


Figure 4.13: (a) thermogravimetric analysis profiles of all CLCNOs, (b) first-order derivative weight loss curves of all CLCNOs.

The data showed that the decomposition of this material occurred in two stages. These stages of decomposition are shown by the peak at 738 $^{\circ}\text{C}$ and the shoulder at 830 $^{\circ}\text{C}$. This two stage decomposition was also seen for p_{cod} CLCNOs (710 $^{\circ}\text{C}$, 832 $^{\circ}\text{C}$).

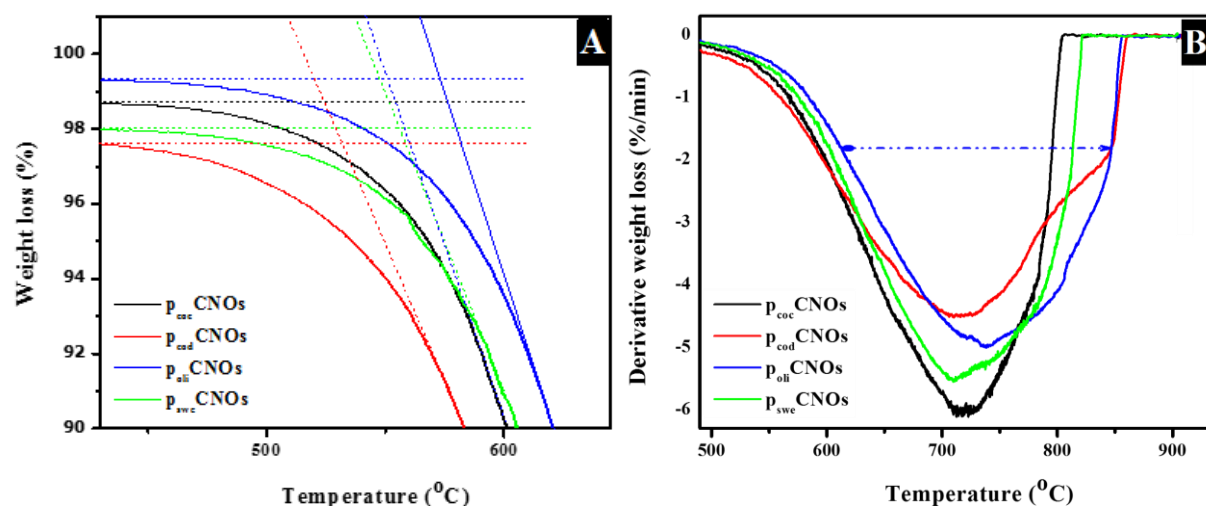


Figure 4.14: Zoomed; (a) thermogravimetric analysis profiles of all CLCNOs, (b) first-order derivative weight loss curves of all CLCNOs.

In summary, the observed TGA profiles and DTA curves for all as-synthesized CLCNOs reveal structural architectural information that corroborated with the Raman and high resolution TEM

results. This suggests that structural architectural information can be explained by considering the “*snow fall*” growth process, as described in **Section 4.4.1**.

4.5. Conclusions

The synthesized CLCNOs are mainly found as non-metallic quasi-spherical nanoparticles. This carbon allotrope has nanoparticles that have particle sizes less than 80 nm and also exhibit concentric multi-layers. Moreover, the results show the presence of short-range order of the turbostratic multi-layers. However, the number of shells exhibited by all as-synthesized CLCNOs could not be determined. These carbon nanoparticles are mostly connected like chains in which they have surface fragmentations as shown by TEM results. CLCNOs synthesized by flame pyrolysis process are mainly polycrystalline nanomaterial following their “*snow fall*” growth process as presented by the two peak appearances in the PXRD diffractograms. They can be classified as nanomaterial exhibiting unique chemical properties since they bare surface functional groups. As confirmed by FTIR, their surface functional groups are attributed to the breaking down of the branched molecular structures from the oil precursors into reactive PAHs during pyrolysis. This was further confirmed by the higher I_D/I_G obtained from higher D-bands FWHMs for all samples. Moreover, the higher D-bands FWHMs revealed that all samples are defective with the increasing defects density as $p_{coc}CLCNOs > p_{cod}CLCNOs > p_{oli}CLCNOs > p_{swe}CLCNOs$ indicating the presence of disordered short ranged layers. Furthermore, the morphology or structural properties presented similar thermal strength and decomposition.

This study also indicated that the CLCNOs properties such as surface area and pore volume also depend on the type of precursor oil used. Notably, the highest surface area among the four CLCNOs materials was obtained from $p_{oli}CLCNOs$. This is an important property for application purposes, as such, in further studies, the CLCNOs obtained from olive oil were used, due to their smaller particle sizes and higher content of oxygen carrying surface functional groups.

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CHAPTER 5

The selective synthesis of carbon nano-onions using olive oil and their application in chemiresistive gas sensors for detecting acetone, chloroform, ethanol and toluene.

5.1. Introduction

Carbon nano-onions belong to a family of fullerenes and they are classified as one of the spherical carbon nanomaterials. Their structural architecture is made of concentric multiple-layered fullerenes with layers arranged similar to that of onion rings. They are mainly composed of sp^2 or sp^3 hybridized carbon atoms that are arranged to form the concentric multi-layered quasi-spherical carbon nanostructures [1]. These graphitic nanostructures are similar to the spheroidal nanoparticles discovered and described by Iijima [2, 3]. They possess fascinating and unique chemical and physical properties such as a high electrical conductivity and a large surface area [4, 5]. Their synthesis involves the use of various methods such as thermal annealing of nanodiamonds [6], arc-discharge [7] as well as pyrolysis [8] in which different shapes and sizes of CNOs can be obtained (e.g. hollow CNOs, <50 nm) [9, 10].

In 2012, Choucair and Stride reported on a pyrolysis method for the production of carbon nano-materials (CNMs). The method adopted is inexpensive and makes use of a simple apparatus along with readily available carbon sources [11]. Later, Hamid *et al.*, reported on the catalysed spray pyrolysis of oxygen containing organic compounds as an inexpensive alternative method to synthesize CNMs such as carbon nanotubes [12]. Several carbon sources such as paraffin oil, flaxseed oil and naphthalene have been reported for the synthesis of stable CNOs using an open flame pyrolysis method [13-16]. This method can readily be scaled up for the production of CNOs to produce clean CNOs. Oils derived from different plants (e.g. grapeseed oil) mainly consist of aliphatic long chain fatty acids and hydrocarbons [17, 18]. Their incomplete combustion easily leads to the formation of CNOs. The recent report by Jung *et al.*, reveals that CNOs have been synthesized using a waste frying oil as the carbon source in the pyrolysis process [19]. Similarly, olive oil can be regarded as one of the useful oils that can produce CNOs that exhibit fascinating chemical properties [20, 21]. It is known that olive oil exists as three common types, namely; olive

pomace oil, refined olive oil, and virgin olive oil. They are produced by different processing methods and this provides oils with different chemical compositions [22]. The existence of different oxygen species in the chemical composition of olive oil as shown in **Figure 5.1** leads to interesting chemical properties that suggests its use as a hydrocarbon source for the production of oxygenated CNOs [23].

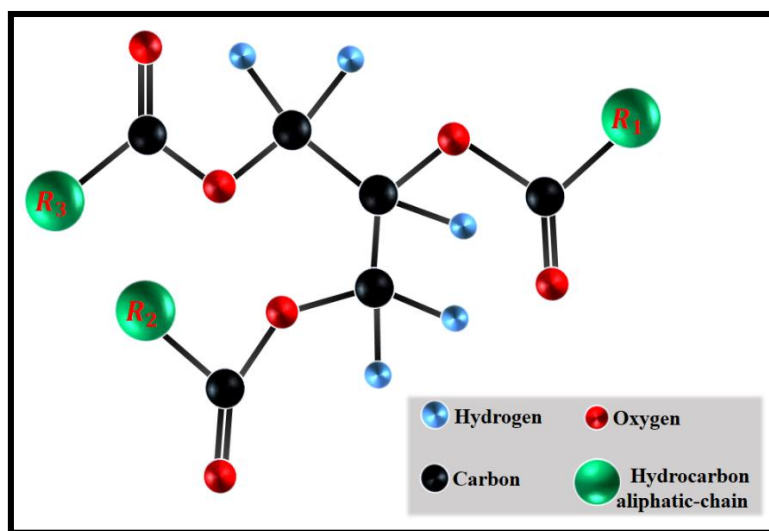


Figure 5.1: The general molecular chemical structure of olive oil [19, 20, 23].

The ease of synthesizing CLCNOs using olive oil allows for their use in various applications including their use as a gas sensing active material when made as a composite [24-29]. In this study, olive oil was selected as the carbon precursor due to; (i) its ease of combustion, and (ii) its availability of different chemical configurations of oxygen atoms in its molecular structure. The oxygen atoms in the CLCNOs derived from olive oil can assist in the use of chemiresistive gas sensors for the detection of volatile organic chemicals (VOCs) [30]. In this study the CLCNOs have been added to manganese dioxide (MnO_2) and a polymer (polyvinylpyrrolidone (PVP)) to make an active sensing material for purposes of VOCs detection at room temperature [30]. In this case, the oxygen species in the structural matrix of CLCNOs could be useful for VOC detection since the sensing mechanism depends on the oxygen concentration on the surface of an active sensing material [31, 32]. Thus, a composite made of oxygenated CLCNOs, MnO_2 and PVP will allow for better adsorption and desorption of oxygen molecules. Moreover, the oxygen containing CLCNOs will further promote charge carriers separation within the metal oxide based carbon nanoparticles composite [33]. Hence, it can be hypothesized that the synergistic activity of the CLCNOs and MnO_2 mixed with

the non-electrical conducting PVP will allow for detection of different VOCs (herein; acetone, chloroform, ethanol, and toluene) at room temperature. To the best of my knowledge, this is a first time report on the use of olive oil derived CLCNOs for this kind of application. However, there has been related studies conducted using different carbon nanoparticle composites to detect various VOCs (e.g. 2-methylcyclopentanone) [34].

5.2. Experimental

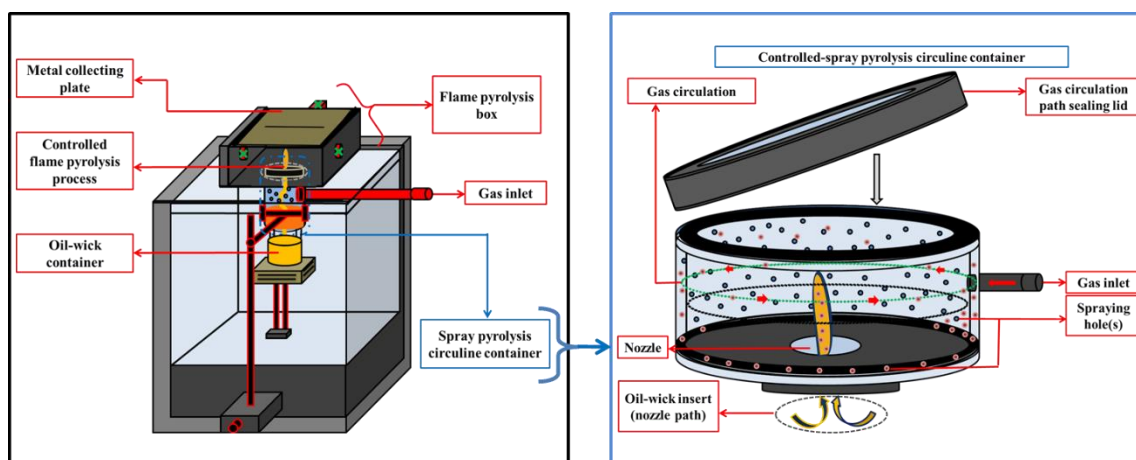
5.2.1. Starting materials

Common essential olive oil produced by the Hercules Company (Durban, South Africa) and a fibre-glass wick (purchased from a local retailer) were used as received. A polished brass collecting plate (BCP, size: 140×140×1.5 mm) and a steel-tube stand (see **Scheme 5.1**) designed with a circular shaped air-flame controlling ring were built in the University of the Witwatersrand Physical Sciences Workshop. The compressed air was purchased from Afrox Company (Johannesburg, South Africa). Acetone, air, chloroform, ethanol, hexane, manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), polyvinylpyrrolidone (PVP), potassium permanganate (KMnO_4) and toluene were purchased from Sigma Aldrich/Merck and were used as received.

5.2.2. Synthesis of CLCNOs using olive oil

Olive oil (10 mL) was transferred into a 20 mL glass container in which a fibre-glass wick was immersed and allowed to stand in the oil for 45 minutes such that it extracted the oil by capillary action and/or surface tension [35]. The glass container was placed beneath the acetone washed BCP as shown in **Scheme 5.1**, at an optimized distance of ~40 mm between the glass nozzle and the BCP using a distance adjusting rod. Finally, the distance between the luminous zone of the flame and the collection plate was maintained at ~20 mm. The wick was ignited to produce a flame at room temperature in air. In a typical experimental process, a circular ring shown in **Scheme 5.1** was used to control the flame shape by flushing synthetic-compressed air around the ring's circular path that has air-spraying holes. The as-synthesized product from the olive oil was then collected continuously onto to BCP plate for 15 minutes. This was followed by collection of the product by scraping the black carbonaceous powder from the BCP using a solid-plastic spatula. The collected CLCNOs were washed with hexane in a Soxhlet extractor to remove excess oil from the carbon

nanomaterial sample. The final product was labelled $p_{oli}CLCNOs$, for CLCNOs synthesized using olive oil.



Scheme 5.1: The flame pyrolysis set-up used during the olive-oil flame pyrolysis process with detailed controlled-spray pyrolysis circular container for controlling the flame shape.

5.2.3. Synthesis of metal oxide nanorods

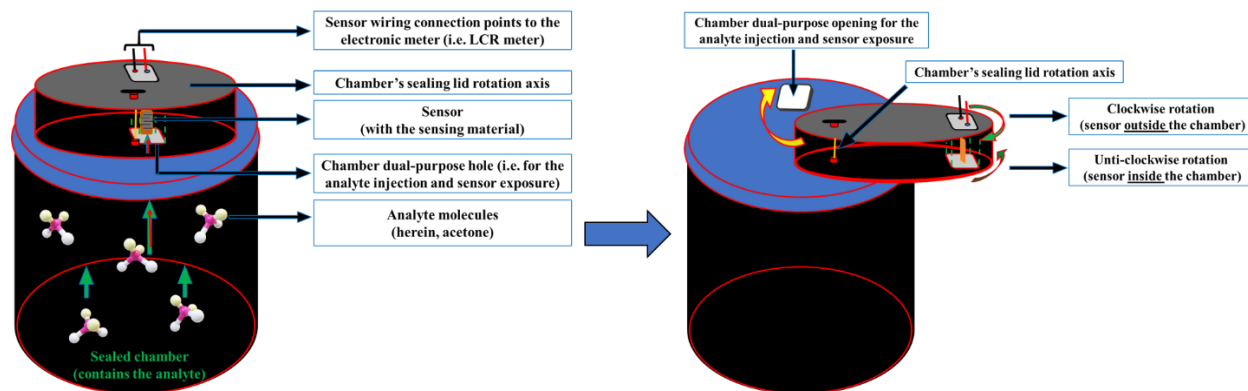
Manganese dioxide nanorods (MONR) were synthesized using a method previously reported by Wang *et al.*, without any modification [36]. About 0.63 g of $KMnO_4$ and 0.25 g of $MnSO_4 \cdot H_2O$ were mixed and stirred in 40 mL distilled water (dH_2O) to form a homogeneous solution. The solution was transferred into a Teflon-lined autoclave for the hydrothermal synthesis of the MONRs. The Teflon-lined hydrothermal autoclave was heated up to 160 °C and the reaction continued for 12 h. After completing the reaction, the autoclave was then allowed to cool to room temperature and the product was collected as a brown precipitate. This was followed by centrifugation of the collected precipitate using ethanol and dH_2O as alternating solvents, at 1400 rpm for 15 min. The obtained final-product (MONR) was then dried at 80 °C for 24 h in a vacuum oven.

5.2.4. Fabrication and testing of the sensing devices

The initial step involved the preparation of a mixed materials solution (i.e. composite solution), using $p_{oli}CLCNOs$, manganese dioxide nanorods (MONRs), polyvinylpyrrolidone (PVP) and

dimethylformamide (DMF). DMF was used as the preferred solvent due to its ability to disperse MONRs together with CLCNOs. PVP was then used to stabilize the MONRs under room temperature conditions. The three materials composite was prepared using 1:1:3 ratio of CLCNOs:MONRs:PVP added to 3 mL of DMF. The mixture was stirred for 12 h at room temperature followed by sonication for 1 h to obtain a homogeneous suspension of the composite. Electrodes used for the device fabrication were cleaned following a standard procedure. Typically, the inter-digitated electrodes (IDEs) with a total of 40 strips (strip thickness: $\sim 72\ \mu\text{m}$ thickness, the distance between the strips: $\sim 130\ \mu\text{m}$) were firstly cleaned using acetone, distilled water and isopropanol in 20 minute sonication steps. The cleaning process was followed by drying of the IDEs in a vacuum oven at $100\ ^\circ\text{C}$ for 45 minutes. Every composite solution was drop casted onto the dry inter-digitated electrodes (IDEs). A micropipette was used to drop cast $10\ \mu\text{L}$ of the composite solution onto different IDEs to give a poliCLCNOs -based sensing device. The resulting sensor was vacuum dried at $100\ ^\circ\text{C}$ for 30 minutes, kept in a desiccator and labelled as pS.

The fabricated sensor was tested using the Agilent 4284A Precision LCR meter instrument. Selected frequencies (i.e. 1, 3, 6, 10 and 20 kHz) were used during the tests along with resistance measurements. The prepared sensors were tested using $1\ \mu\text{L}$ per injection of analyte using a 2.4 L analysis chamber; this gave various concentrations of the different analytes (i.e. acetone, chloroform, ethanol and toluene) calculated using **Formula 2.1** following the blank measurement (i.e. measurement at $0\ \mu\text{L}$ (0 ppm, no analyte)) [37]. During every test, $1\ \mu\text{L}$ of the analyte was injected into the chamber system. The chamber was designed in a manner that allowed for analyte injection and sensor exposure in the different environments (see **Scheme 5.2**).



Scheme 5.2: Chamber designed with a set-up used during all electro-chemical tests.

All tests were conducted in a sealed glove box environment in which the relative humidity (RH) was maintained at 27%. The RH below 30% (i.e. kept at 27%) was constantly monitored by using a constant flow of nitrogen at 300 sccm that was considered as a diluting purging gas used to limit and/or reduce high moisture contents (i.e. RH: >30%) that can affect the analyte detection at 25 °C. Moreover, it is important to keep less moisture content such that water (H₂O) molecules do not cloud in dominance over any sensing device environment (i.e. in the testing chamber or glove box). Thus, a sweep cover on the chamber lid was additionally used to locate the sensor inside or outside the analytes' environment (i.e. in the chamber with analyte or the in the nitrogen controlled glove box environment) as shown in **Scheme 5.2**. The resistance as a function of frequency measurement was conducted to select the best working frequency for the sensing device. This was done by injecting 1 µL of analyte into the chamber until 5 µL was reached, in which the sensor was exposed for 150 seconds towards increasing analyte concentrations (i.e. at intervals of 1 µL). Thus, any changes in frequency were measured by comparing the strength of the blank signal divided by the background noise of the blank signal over the same time and this lead to the determination of the signal-to-noise ratio (SNR), (**Formula 2.3**) [38].

The sensitivity (S_s) and the limit of detection (LoD) were calculated using **Formula 2.4** and **2.5** respectively. The sensitivity of a sensing device, was calculated from the slope of a calibration curve which is the change in the sensor response per concentration of the analyte. This is obtained from the first derivative of the response (herein; the response R is the relative resistance variation $R = \Delta R/R_o$), with respect to the concentration of the analyte [39, 40]. The lowest amount of analyte in the detection system that can be detected and that is significantly different from the blank, but not necessarily quantified under stated experimental conditions, was estimated using the LoD formula (**Formula 2.5**) [41, 42].

5.3. Techniques used to characterize the nanomaterials used to form the sensing material

The morphology and characteristics of the CLCNOs produced were studied using the scanning electron microscopy (SEM) technique and the instrument FEI Nova Nanolab 600 FIB-SEM was operated at 30 kV. The microscopy micrographs of the CLCNOs and the metal oxide based

composite were ascertained by transmission electron microscopy (TEM) using a Tecnai G2 30ST operating at 200 kV. The quality and structural properties of CLCNOs (supported on a silicon wafer (2 mg sample holder)) and its metal oxide composite were investigated using a Jobin-Yvon T64000 Ultraviolet (UV) LabRam HR-micro Raman spectrometer. This contained an Olympus BX41 microscope that made use of a liquid nitrogen cooled charge coupled device detector working at an excitation wavelength of 514.5 nm at room temperature. A Bruker D2 Phaser XRD that used Cu-K α irradiation and operated at 30 kV with the X-ray tube at the current of 30 mA over a $10^\circ \leq 2\theta \leq 90^\circ$ scanning range gave information on the crystallographic nature of the CLCNOs based samples. A Micromeritics Tristar 3000 surface area and porosity analyser was used to determine the surface area and pore volume of the CLCNOs (200 mg). The elemental composition of the CLCNOs and its metal oxide composite surface analysis was achieved using two different techniques. These were SEM/EDS and XPS. A FEI Nova Nanolab 600 FIB-SEM instrument as well as the FEI Quanta 450 FEG-SEM coupled with the energy dispersive spectroscopy (EDS) detector was used to determine the structural morphology of CLCNOs and their surface elemental composition. A Physical Electronics Quantum 2000 X-ray photoelectron spectrometer that used a monochromatic Al K α source operated at 1486.7 eV gave surface information.

5.4. Results and discussion

5.4.1. Structural morphology analysis of the CLCNOs

The SEM micrograph shown in **Figure 5.2(a)** revealed that the as-synthesized material exhibited carbonaceous nanoparticles that were clustered together. The nanoparticles formed in this study have particle sizes of less than 80 nm. It can be seen that these nanoparticles are connected to form larger carbon-aggregates (CAs). As depicted in **Figure 5.2(b)**, it can be seen that the material contained primary particles (PPs) with various sizes similar to those of the diesel soot particles as previously reported by Leidenberger *et al.* [43]. The CAs formed from the poly-aromatic hydrocarbon radicals were mostly connected in chains. It was also observed that the PPs formed various CAs that had quasi-spherically shapes and mostly overlapped with each other. This can be attributed to nuclei coalescence that occurred during the combustion or pyrolysis process [44, 45].

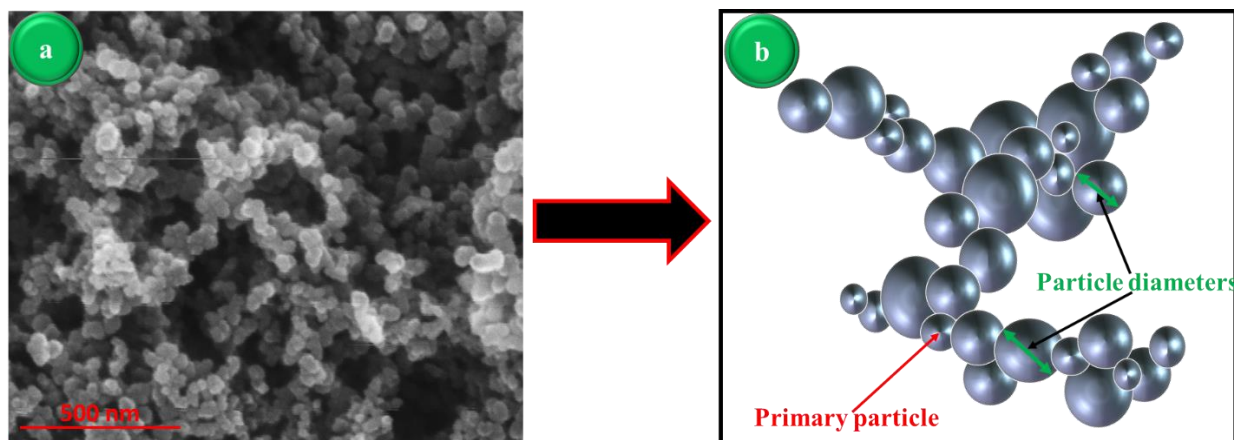


Figure 5.2: (a) SEM micrograph of the produced CLCNOs using olive oil (i.e. p_{oli} CLCNOs), and (b) schematic representation of p_{oli} CLCNOs conglomerate.

Figure 5.3(a) also showed the two dimensional (2D) micrographs of conglomerated CLCNOs nanoparticles that support the SEM results. The quasi-spherical nanoparticles formed by pyrolysis always formed larger carbon-aggregates that are connected in chain form. Hence, in this study, the name given to the material is; ‘chain-like carbon nano-onions (CLCNOs)’. The quasi-spherical nanoparticles formed have different sizes that promote their overlap. The particle sizes distribution curve shown in **Figure 5.3(b)** shows that, this material has nanoparticles that are less than 80 nm (i.e. 55 ± 3.3 nm) [46].

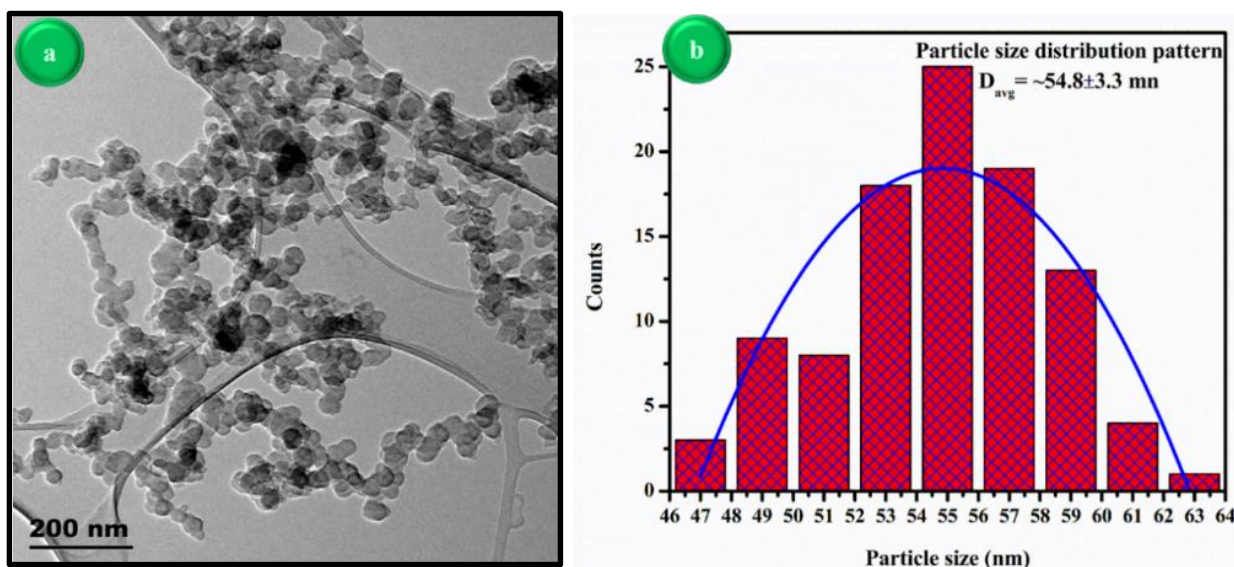


Figure 5.3: (a) low magnification TEM micrograph of as-synthesized CLCNOs using olive oil (i.e. p_{oli} CLCNOs), and (b) particle size distribution curve of p_{oli} CLCNOs.

It is also evident that the CLCNOs particles overlap with one another to form carbon aggregates as shown in **Figure 5.4(a)**. Hence, in this material, it is difficult to observe single nanoparticle and/or even obtain mono-dispersed CLCNOs particles. Thus, the micrograph shown in **Figure 5.4(b)** indicates that every CNO particle exhibits two distinct multi-layered regions. It can be seen that there exists an inner core and an outer shell. The inner core contains a number of short-range multi-layers (see **Figure 5.4(b)** and **Scheme 5.3**).

The observed multi-layers cover the nucleus of each nanoparticle, with an inter-layer spacing of ca. ~ 0.35 nm. On the other hand, the outer shell is composed of disordered multi-layers that are mostly found near or on the external outer surface of the CLCNOs. However, some amorphous and graphitic crystallites can be found in the outer shell regions, which promotes the turbostratic nature of these nanoparticles. Thus, it can be suggested that these disordered multi-layers are ascribed to surface fragmentations. The CLCNOs surface is rough due to the defective sites on the nanoparticle surface.

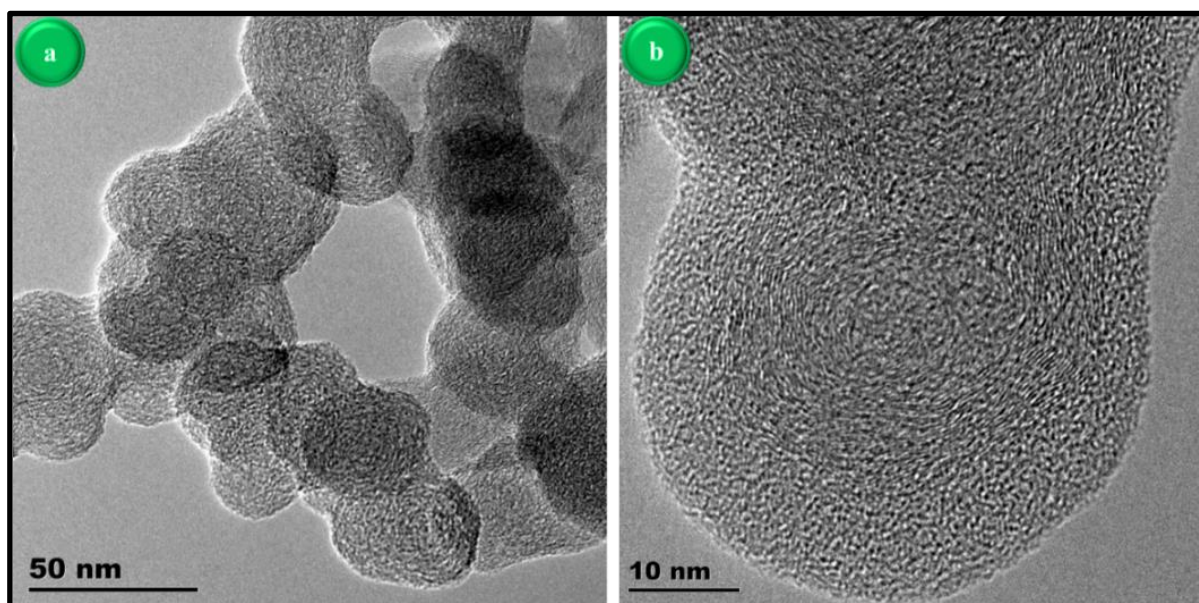
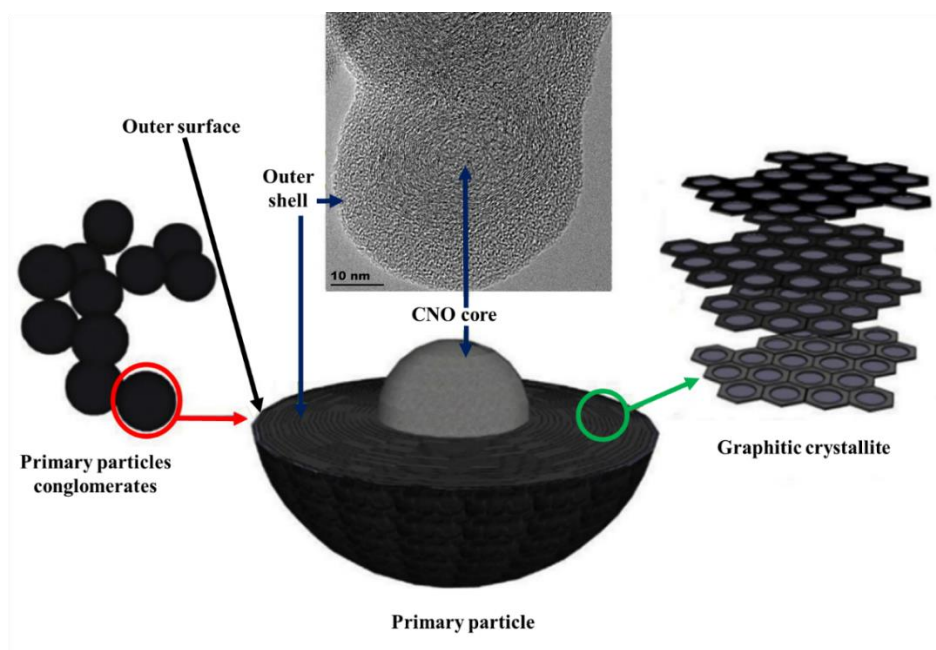


Figure 5.4: High magnification TEM micrograph of; (a) chain-like connected $p_{cli}CLCNOs$, and (b) $p_{cli}CNO$ nanoparticle with short range multi-layering.



Scheme 5.3: Description of the conglomeration of various multi-layered primary particles with a dense core [47].

Figure 5.5 shows the composite mixture formed from $p_{oli}CLCNOs$ and MONRs. It is evident that the MONRs were formed successfully following the method reported by Wang *et al.*, (see **Figure 5.5(a)**) [36, 48]. The as-synthesized MONRs exhibit different sizes and/or lengths, which allow for various packing arrangement in the $p_{oli}CLCNOs$ composite. In addition, **Figure 5.5(b)** shows that the structural shapes of CLCNOs are maintained in the $p_{oli}CLCNOs$ -MONRs based composite formed by the physical mixing of these materials (arrow number two). The composite is formed by the MONRs (see arrow number one in **Figure 5.5(b)**) that are partly supported onto $p_{oli}CLCNOs$. Thus, the $p_{oli}CLCNOs$ particles also contribute to connecting the MONRs surfaces.

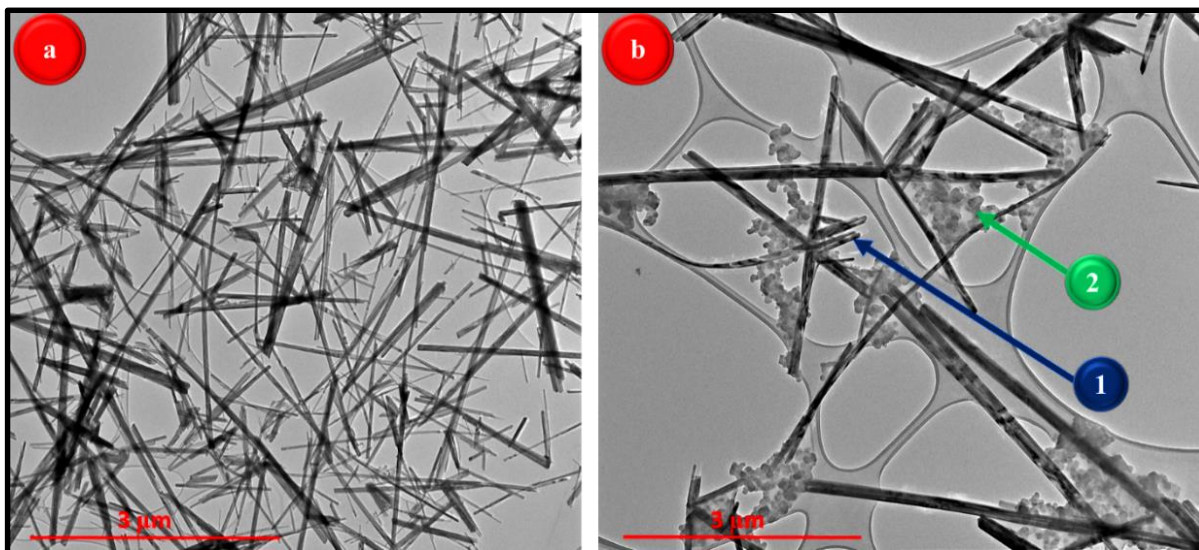


Figure 5.5: Low magnification TEM micrograph of; (a) as-synthesized MONRs, and (b) MONRs/poliCLCNOs composite.

The elemental composition of the poliCLCNOs-MONRs based composite was investigated using the EDS analysis technique. It is evident from the EDS spectra shown in **Figure 5.6** reveal that both materials analysed contained carbon. The EDS spectrum obtained from the highlighted region shows that the analysed area only contained carbon nanoparticles as shown in **Figure 5.6(a)**. However, the other detected carbon content can be from the carbon tape that was used during analysis which is unavoidable when using SEM. Furthermore, it was suggest that the kind of carbonaceous nanoparticles obtained exhibit oxygen atoms on their surfaces. Therefore, the appearance of the oxygen peak appearance is attributed to the carbonyl groups provided by the olive oil as the pyrolysis carbon source. On the other hand, the EDS spectrum shown in **Figure 5.6(b)** indicates that the composite is formed by carbon, oxygen and manganese. There are two types of manganese detected namely α -Mn and the β -Mn. Thus, it can be suggested that the composite contains the α -MONRs and the β -MONRs in accordance to the EDS analysis area used.

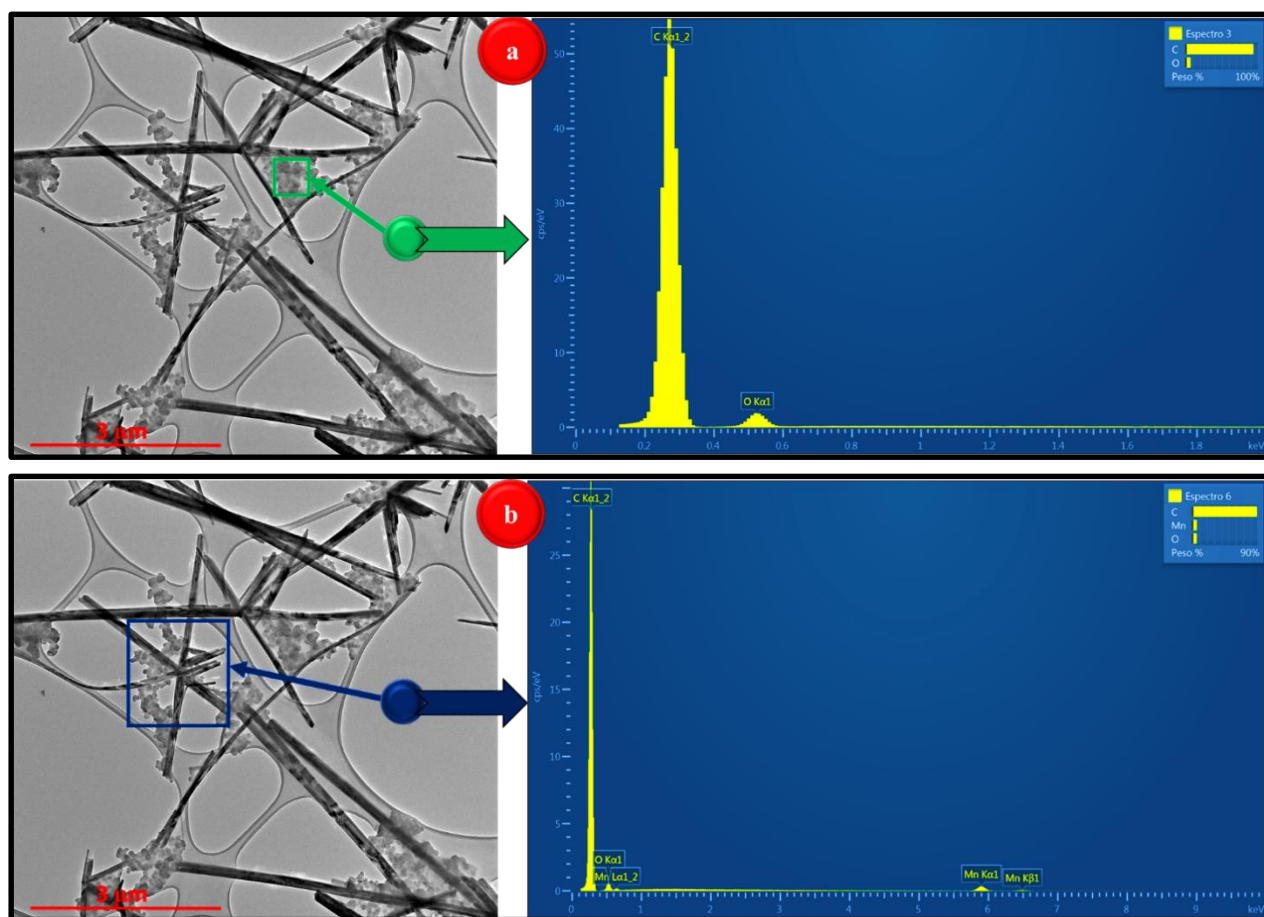


Figure 5.6: The EDX spectrum and low magnification TEM micrograph of; (a) as-synthesized poliCLCNOs with MONRs, and (b) MONRs/poliCLCNOs composite.

To supplement the results obtained through SEM and TEM analysis, Raman spectroscopy was used to further analyse the degree of atomic order in the structural matrix of the nanoparticles formed. **Figure 5.7(a)** shows the two Raman prominent peaks, commonly known as the D- and G-bands, for carbonaceous nanomaterials. The peaks observed around 1338 cm^{-1} are commonly labelled as the D-band, representing the density of induced disorder from C–C vibrations modes corresponding to the disruptions in sp^2 bonding to form newly hybridized carbon bonds such as dangling bonds, sp^3 bonds etc. [49]. This band can also signify the presence of structural vacancies, and carbon rings other than hexagons [49]. The observed peak around 1586 cm^{-1} is labelled as the G-band and is ascribed to the C=C graphite carbon in-plane vibration modes of a carbon material with sp^2 orbital structure [50].

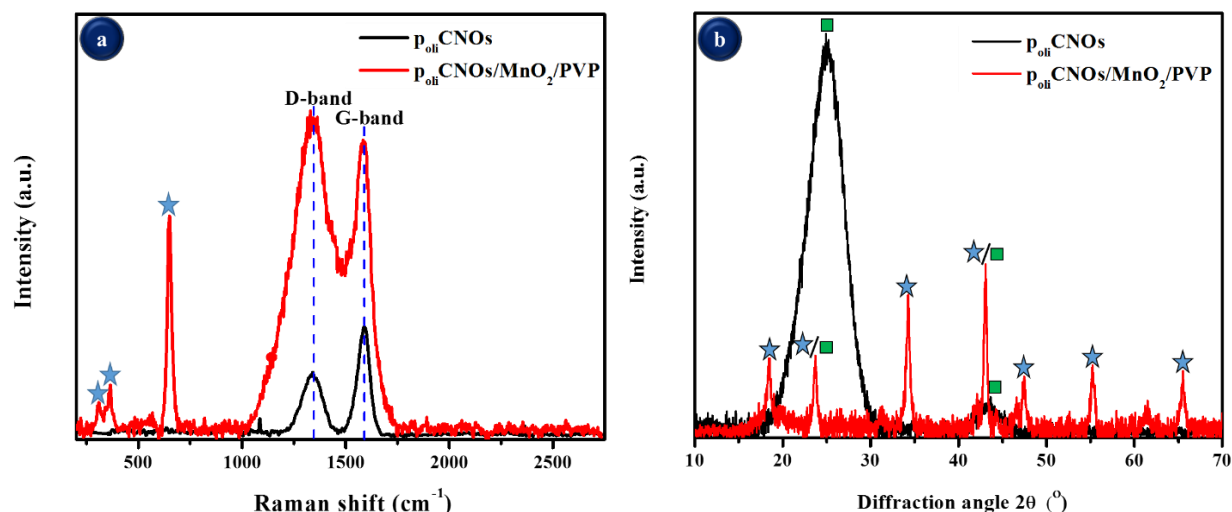


Figure 5.7: (a) the Raman spectra of as-synthesized MONRs, and (b) MONRs/p_{oli}CLCNPs-PVP-based composite, and (b) PXRD patterns of as-synthesized β-MONRs, and (b) β-MONRs/p_{oli}CLCNPs/PVP-based composite.

The D- and G-band full width at half maximum (FWHM) were ca. 90 and 50 respectively for both samples as shown in **Table 5.1** with the G-band FWHM for both samples lower than those of the D-bands. Both samples presented sharp G-bands even though they showed different intensities (see **Figure 5.7(a)**). Thus, it suggests that the p_{oli}CLCNPs and its composite exhibit sp² hybridized carbon atoms. In addition, the results in **Table 5.1** indicate that the D-band FWHMs are higher than those of the G-band and this can be attributed to the increased amount of sp³ C-C vibration modes which can also indicate structural disorder. Moreover, this observation can be attributed to the exposure of the in-plane terminations of either a pentagonal or hexagonal carbon network of the p_{oli}CLCNPs outer shell as well as amorphous carbon impurities [50].

The area ratios of the D-band and the G-band (I_D/I_G) can be used to quantify the degree of graphitization of the as-synthesized p_{oli}CLCNPs and p_{oli}CLCNPs in the composite [50]. It can be seen that the I_D/I_G values for both samples are greater than 1 as shown in **Table 5.1**. This implies a low degree of graphitization, ascribed to long-range structural disorder of the carbon nanoparticles [51]. It was observed that the defect density increased in the p_{oli}CLCNPs/MONRs/PVP composite since the I_D/I_G ratio (i.e. ca. 2.95) was more than double as compared to the as-synthesized p_{oli}CLCNPs (ca. 1.21). This further suggests that the physical mixture of the composite contained more nanoparticulate structural defects. Moreover, the

increased defect density in the composite is attributed to the presence of MONRs and PVP as shown by their peak appearances below 750 cm^{-1} in **Figure 5.7(a)**. **Figure 5.7(b)** shows the PXRD patterns for p_{oli}CLCNOs and its MONRs composite in which the bare p_{oli}CLCNOs pattern presents the two prominent peaks for the polycrystalline carbon material at around 24° and 43° . These peaks can be assigned to the 002 and 004 planes of carbon nanoparticles. Thus, the appearance of peak centred at $2\theta \approx 43^\circ$ signifies that the CLCNOs produced contain moderate graphitic carbon domains. Moreover, the PXRD pattern for the composite presents multiple peaks which signify the presence of β -MONRs (**Figure 5.7(b)**).

Table 5.1: Raman data of p_{oli}CLCNOs and p_{oli}CLCNOs/MONRs/PVP composite.

Sample	Raman shift (cm^{-1}) D-band	Raman shift (cm^{-1}) G-band	I_D/I_G	FWHM D-band	FWHM G-band
p _{oli} CLCNOs	1338.3	1585.8	1.21	97.7	60.3
p _{oli} CLCNOs/MONRs/PV P	1337.7	1586.4	2.95	224.7	89.9

I_D : area of the D-band, I_G : area of the G-band, I_D/I_G : ratio of the areas (i.e. for D-band and G-band respectively).

The XPS of p_{oli}CLCNOs was measured and revealed the presence of carbon and oxygen atom (see **Figure 5.8**) [52]. Firstly, the deconvoluted C1s peak presents different C atom bonding configurations in the p_{oli}CLCNOs (**Figure 5.9(a)**) [53, 54].

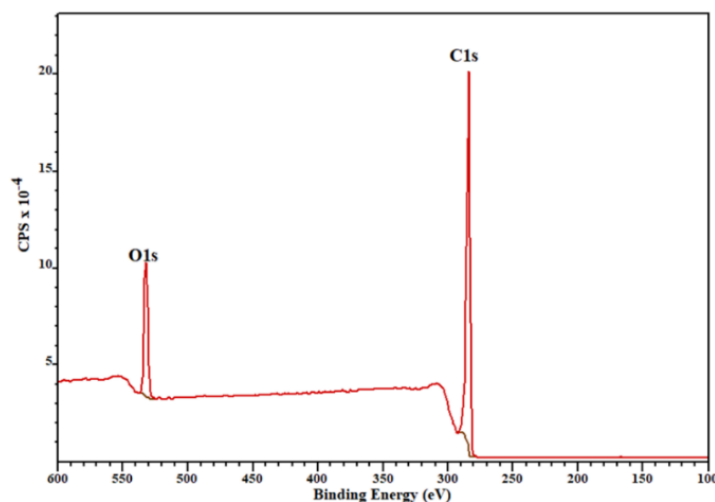


Figure 5.8: The XPS survey scan of p_{oli}CLCNOs synthesized using essential olive oil.

The results in **Figure 5.9(a)** reveal the presence of C-C, sp^3 -C, C-O and O-C=O at the peaks positioned at 283.86 eV, 284.61 eV, 285.64 eV, and 288.06 eV respectively. The results shown in **Figure 5.9(b)** presents the O1s deconvoluted peak which reveals that the p_{oli} CLCNOs sample contains oxygenated carbon atoms (e.g. carbonyl groups) with different bonding configurations [55, 56]. The nanoparticles produced exhibited different oxygen species on their surfaces including C-OH as well as O-C=O groups as indicated by the peaks positioned at 531.89 eV and 533.28 eV respectively [56, 57].

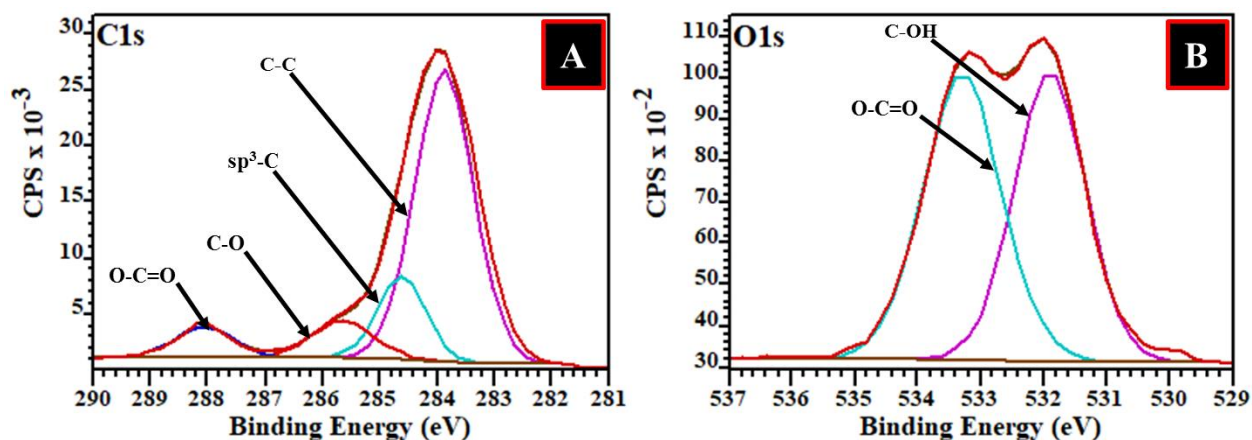


Figure 5.9: The XPS survey scan of p_{oli} CLCNOs' deconvoluted spectrum for; (a) C1s, and (b) O1s that are exhibited by p_{oli} CLCNOs.

The CLCNOs material contain about 88.85% of C and 11.01% of O (see **Figure 5.10**). In addition, the total surface area and pore sizes of the as-synthesized and the composite material were investigated using the BET surface characterization technique [58]. The surface area of p_{oli} CLCNOs (i.e. 68.8 m²/g) was higher than that of its metal oxide based composite (i.e. 19.6 m²/g). The BET measurement further revealed that p_{oli} CLCNOs has pore sizes of 7.38 nm, with a pore volume of 0.17 cm³/g whereas the MONRs sample has a total surface area of 33.3 m²/g with the pore sizes volume of 0.23 nm, and the pore volume of 21.8 cm³/g. Therefore, the pore size and volume were found to be 0.016 nm and 40.1 cm³/g respectively.

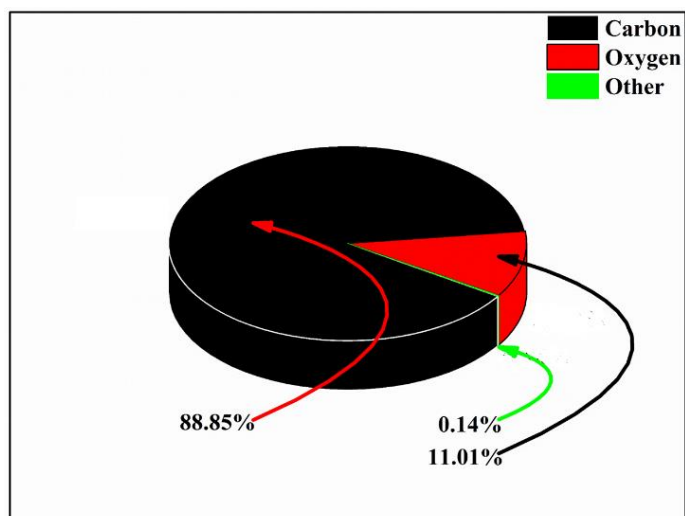


Figure 5.10: The pie chart that represents the XPS survey scan elemental composition percentages of the as-synthesized $p_{oli}CLCNOs$.

5.4.2. Electrochemical tests for detecting different VOCs: Chemiresistance measurements of the $p_{oli}CLCNOs$ sensing device

Investigations towards the chemiresistive response of the $p_{oli}CLCNOs/MONRs/PVP$ composite based sensor for detecting acetone, chloroform, ethanol and toluene vapour were carried out. The IDE allowed for composite spreading between gaps of the electrical conducting strips that are shown in **Figure 5.11**.

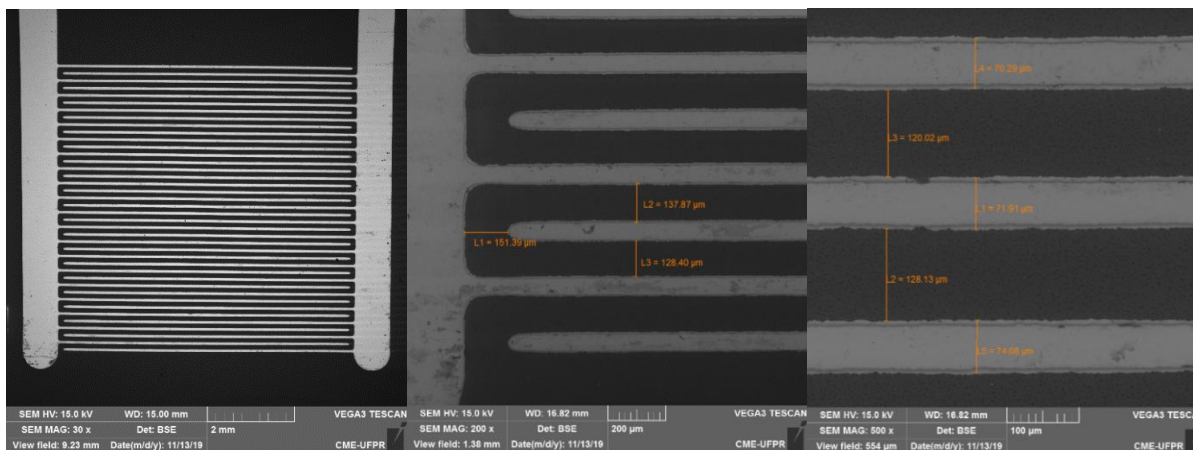


Figure 5.11: SEM image of the IDE used to fabricate the sensing device.

The IDE gaps (in μm) filled with the composite material allowed for electron mobility purposes. With reference to the literature, it can be said that the change in resistance of most sensing devices

does not only depend on the analyte concentration but also on other factors including the signal to noise ratio (SNR) [59]. The static characteristic properties of the sensor allows for selecting the best operating frequency by identifying the highest SNR of the sensing device for the specific VOC [59]. The SNR plot shown in **Figure 5.12** indicates that the prepared sensing device, using the given IDE, had the highest SNR at 10 kHz. Thus, 10 kHz was selected as the optimal working frequency for the detection of all the analytes. The use of this frequency was preferred because it allowed for facile fabrication of a sensing device that makes use of low current [60].

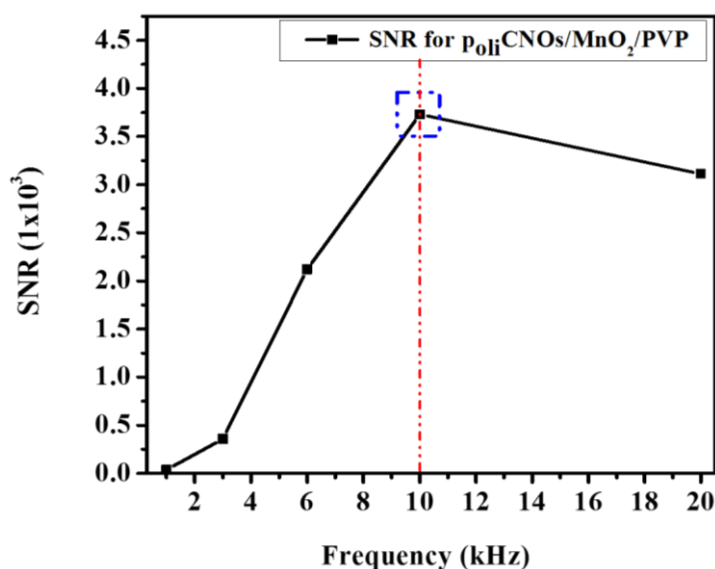


Figure 5.12: SNR plot representing for the sensor fabricated using $p_{oli}CLCNs/MONRs/PVP$ composite.

It is known that sensing devices that are based on metal oxide n-type semiconductors have negative charge carriers as the majority charge carriers and an increase in conductivity occurs in the presence of a reducing gas [61]. Thus, since the composite contains MONRs, the results show that the resistance of the sensor decreased as the concentration of different analytes increased (see **Figure 5.13**). This signifies that the detected analytes exhibit properties (e.g. functional groups) that facilitate molecular interaction with the n-type metal oxide sensing material. A similar response towards different analytes was shown by the decrease in resistance with an increase in every analyte concentration for all tests conducted. The differences in the shape of the baseline i.e. resistance (R) versus frequency (f) curves at 0 ppm are a result of potential kinetically controlled states including the analytes chemisorption and/or physisorption effects.

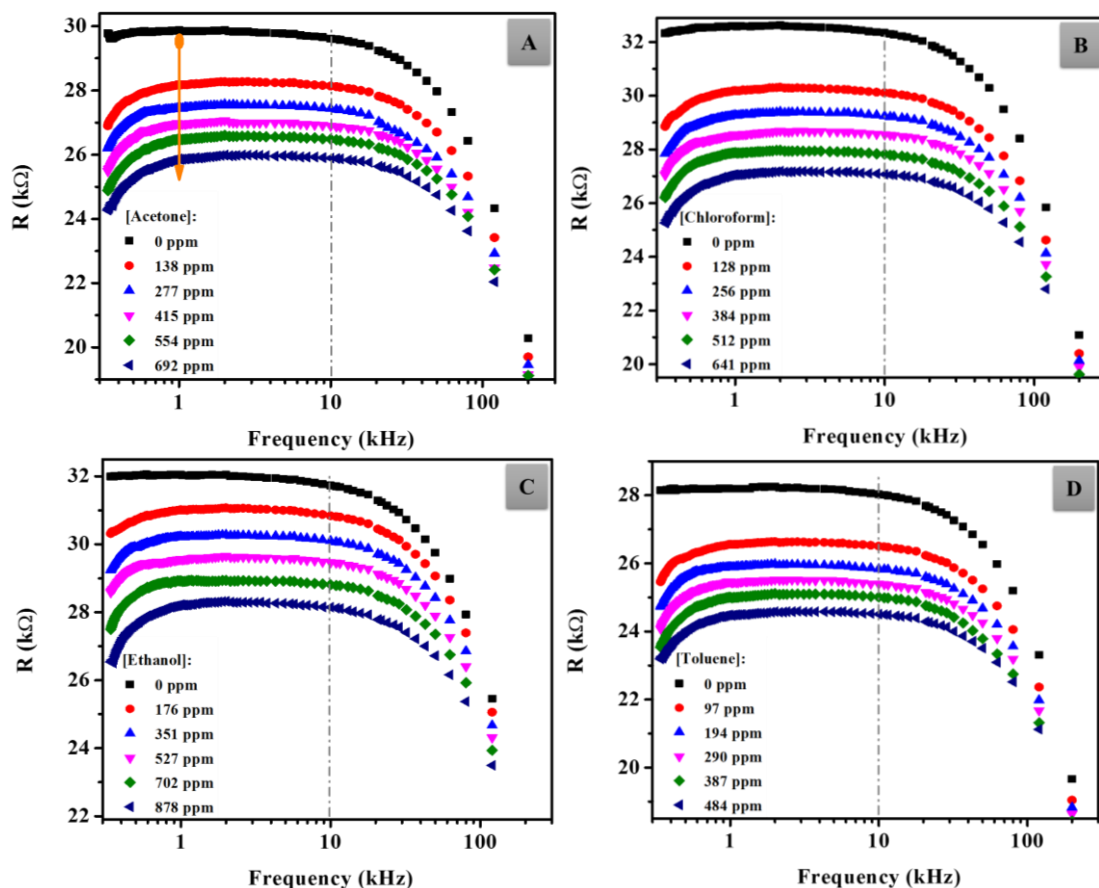


Figure 5.13: Plot of resistance (R in $k\Omega$) as a function of frequency for detecting; (a) acetone, (b) chloroform, (c) ethanol, and (d) toluene, at varied analyte concentrations.

Figure 5.14 also shows a similar shape of the baseline for the blank measurements. The response ($\Delta R/R_0$) as a function of frequency was also measured using different analytes. The results obtained suggest that the adsorption of different analyte molecules on a carbon-based sensing material selectively depends on several parameters. These include the dipole-moment and the surface fragments of the carbonaceous surface that is present in the sensing composite [62]. The results in **Figure 5.14** also show that the resistance decreased as the concentration of different analytes increased which suggests an n-type behavior of the active sensing composite used.

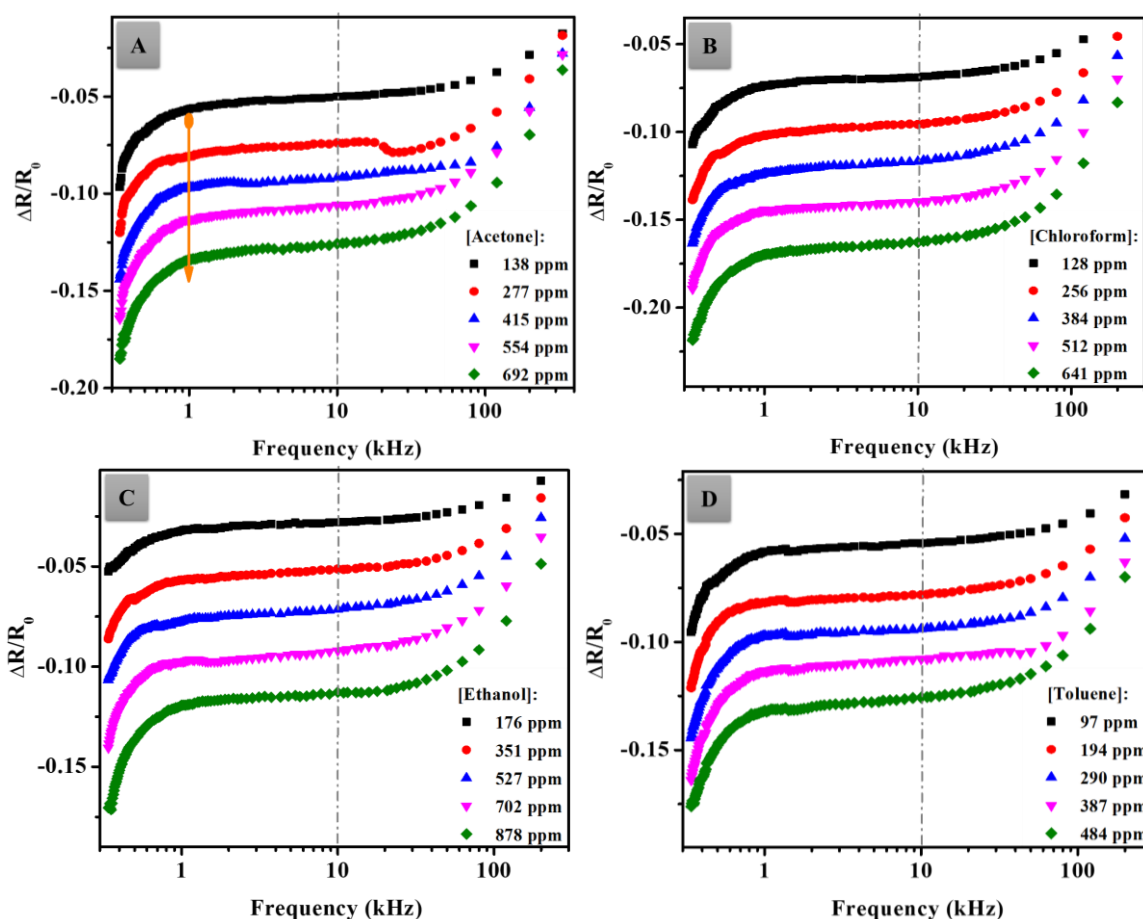


Figure 5.14: Plots of the sensor's response ($\Delta R/R_0$) towards varied analyte concentrations as a function of frequency for the detection of; (a) acetone, (b) chloroform, (c) ethanol, and (d) toluene, at varied analyte concentrations.

As shown in **Figure 5.15**, it can be seen that the response ($\Delta R/R_0$) decreased as the concentration on the analytes increased. These results also showed that the sensing devices used in this study can detect chloroform faster than the other analytes. The detection trend was found to as; chloroform>toluene>ethanol>acetone. The observed trend can be attributed to the electron donating effects provided by each analyte. Chloroform can easily react with active sites on the surface of the sensing composite. Most of the active sites are on the surface interfaces of the poliCLCNOs-aggregates and those of the MONRs. It can be suggested that the ionized surface attached species are responsible for the breakdown of every analyte molecule to adsorb any electron donating groups. These results are supplemented by the observed sensitivities towards every analyte. As shown in **Figure 5.15**, the sensitivity towards chloroform is higher than those of the other analytes.

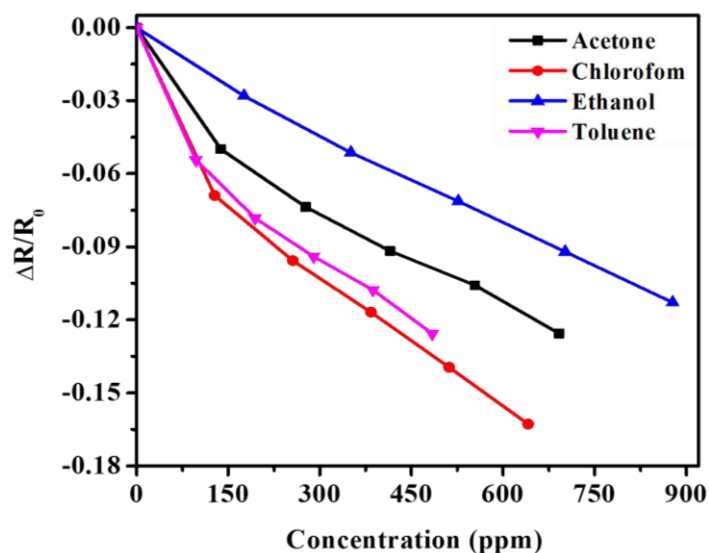


Figure 5.15: The comparison plot for the sensor's response ($\Delta R/R_0$) towards acetone, chloroform, ethanol and toluene as a function of varied analyte concentrations.

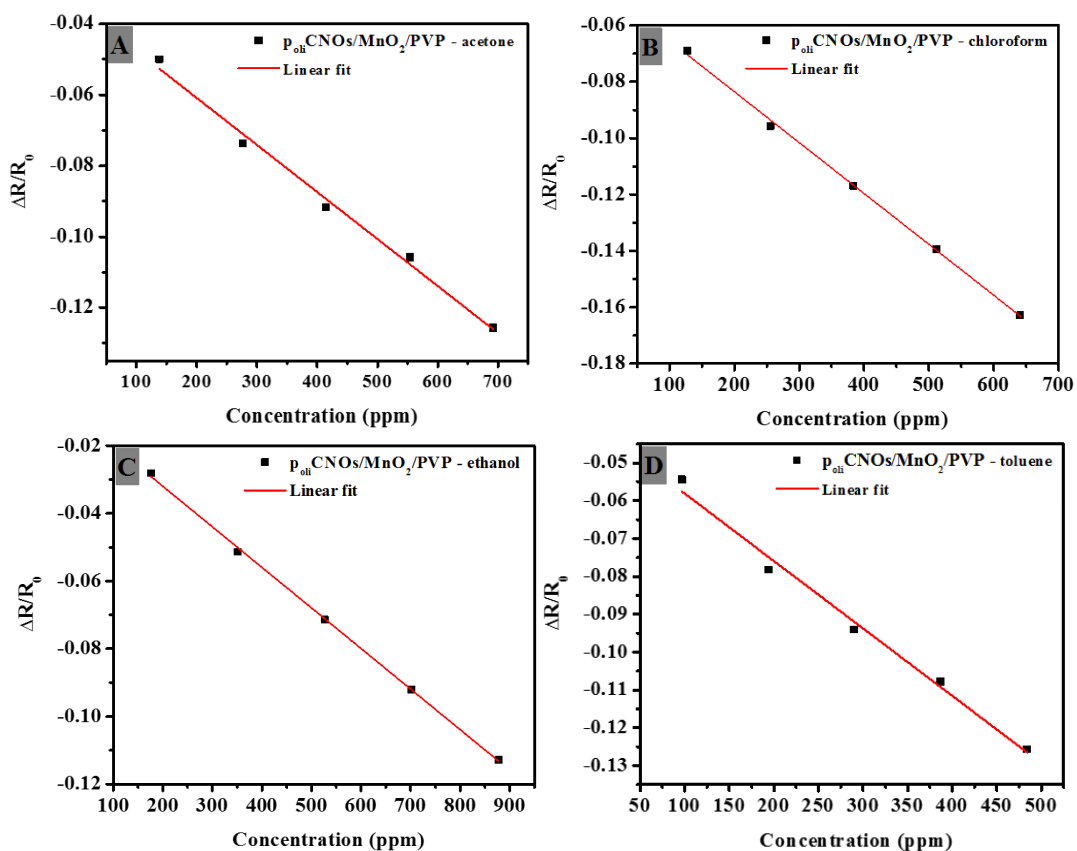


Figure 5.16: Plots that are based on different sensor's response ($\Delta R/R_0$) towards; (a) acetone, (b) chloroform, (c) ethanol, and (d) toluene as a function of varied analyte concentrations with the respective response slopes.

Since it was observed that the resistance and response results obtained revealed an n-type behavior for all sensors as shown by a decrease in resistance with increasing acetone concentrations. This observation was then followed by determinations of the sensitivity of the sensor towards different analytes. The change in each sensor's response to the analyte was determined as the sensor's sensitivity (S) using the slope of a calibration curve. The results in **Figure 5.16** revealed a similar sensitivity towards chloroform and toluene with the sensitivity values of $S_{\text{chloroform}}$: $1.80 \times 10^{-4} \text{ ppm}^{-1}$ and S_{toluene} : $1.78 \times 10^{-4} \text{ ppm}^{-1}$ respectively. However, it was observed that the sensitivity towards acetone and ethanol were lower than those of chloroform and toluene. Hence, the decreasing order of sensitivities towards different analytes was obtained as $S_{\text{chloroform}}$: $1.80 \times 10^{-4} \text{ ppm}^{-1} > S_{\text{toluene}}$: $1.78 \times 10^{-4} \text{ ppm}^{-1} > S_{\text{acetone}}$: $1.33 \times 10^{-4} \text{ ppm}^{-1} > S_{\text{ethanol}}$: $1.20 \times 10^{-4} \text{ ppm}^{-1}$ (also see **Figure 5.18(b)**).

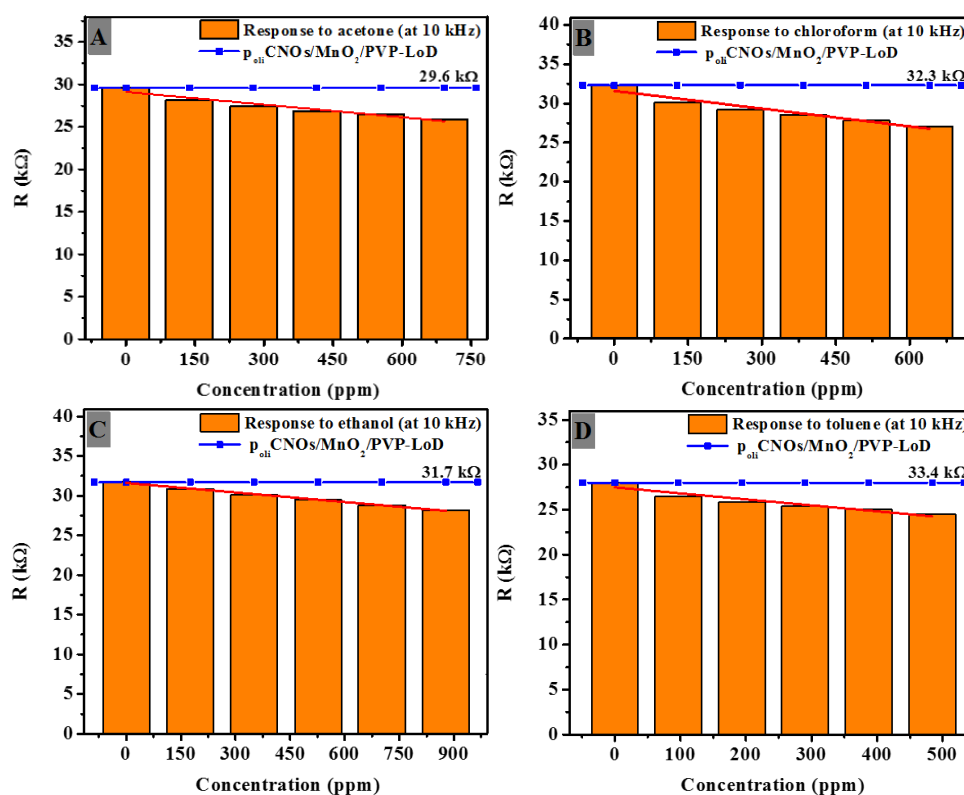


Figure 5.17: The graphs of resistance at 10 kHz as a function of different analyte concentrations, the blue horizontal line indicates the estimated LoD resistance for every measured analyte respectively.

The lowest amount of acetone in the detection system that can be detected and that is significantly different from the blank was determined using the LoD formula (see **Section. 5.2.4**). As shown in

Figure 5.17 and **5.18**, the LoD results for all analytes tested indicated that the lowest LoD is for chloroform (LoD: 1.5 ppm). Furthermore, the data in **Figure 5.18(b)** also reveals that the sensor has the second most sensitivity towards toluene with the second lowest LoD (i.e. 1.6 ppm). This can be associated with the presence of easily available electron donating groups from chloroform and toluene which can be the Cl^- ions and π - π electrons in the benzene ring respectively. These groups easily interact with the active sites on the $\text{p}_{\text{oli}}\text{CLCNOs/MONRs/PVP}$ composite surface edges.

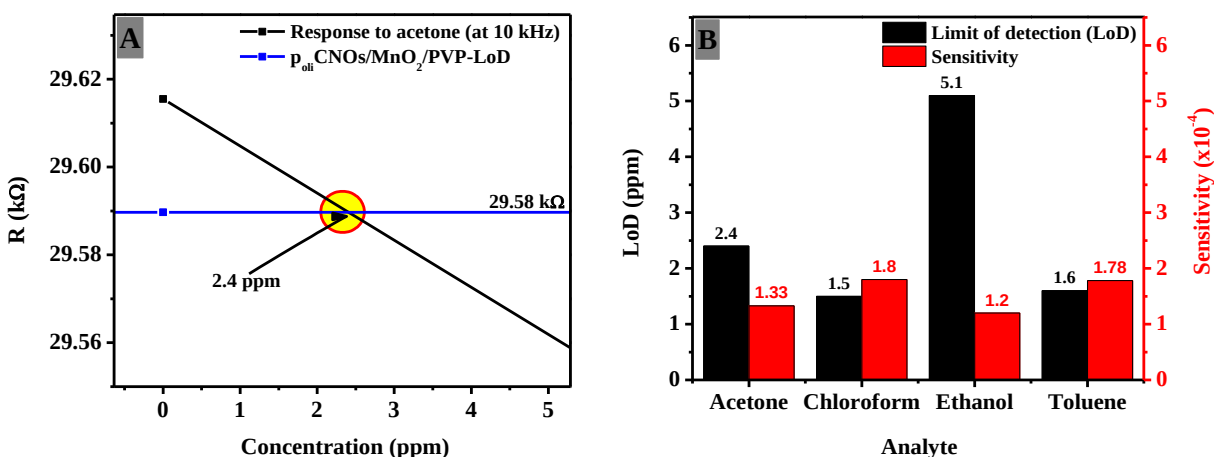


Figure 5.18: The zoomed LoD plot that indicates the regions used to determine the analyte LoD concentration (e.g. 2.4 ppm) with the bar graphs that gives a summary of each analyte LoD and the sensitivity of the sensor.

5.5. Conclusions

Quasi-spherical CLCNOs with particle sizes of ca. 55 nm were synthesized using the essential olive oil as a carbon precursor in the flame pyrolysis process. This carbonaceous material exhibited structural defects including the presence of oxygen containing groups on their surfaces. It is suggested that the physicochemical properties of the $\text{p}_{\text{oli}}\text{CLCNOs}$ and MONRs such as the structural morphology, present surface functional groups influenced the response of the fabricated device towards the detection of different analytes at room temperature. Moreover, the increased defect density in the $\text{p}_{\text{oli}}\text{CLCNOs/MONRs/PVP}$ composite also allowed for better attachment of the molecules from different analytes. Operated at 10 kHz, the gas sensing device showed the lowest LoD and highest sensitivity for better detection of chloroform as compared to the other analytes. This is ascribed to the chloride ions Cl^- from $\text{CH}_3\text{-Cl}$ that attach on the sensing material layer increasing its electron density

which then decreases the resistance. However, the other analytes also exhibit electron donating species (e.g. carboxylic groups) which lead to the increased charge carriers in the sensing material.

Notably, the sensor only responded to different analytes when the three materials (i.e. CLCNOs, MONRs, and PVP) were used to form the active sensing composite. This is attributed to the fact that MONRs cannot work at room temperature unless stabilized by another material such as a polymer and also CLCNOs does not exhibit the required oxygen species (e.g. O_2^-) on their surfaces but only provides good electrical transporting properties. Thus, there exist synergy between the three material and further composite improvements (e.g. use of graphitic carbons) can be useful for enhancing the chemical sensing properties of the sensing layer. Hence, it is proposed that different composites based on tuned carbon nano-onions, and various metal oxide nanoparticles (e.g. MONRs and TiO_2) can be used to further develop inexpensive gas sensing devices in the future.

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CHAPTER 6

The use of ex-situ nitrogen doped olive oil-derived carbon nano-onions for application in chemiresistive gas sensors to detect acetone at room temperature

6.1. Introduction

About four decades ago Iijima reported on multi-layered carbon allotrope with quasi-spherical or spheroidal shape [1, 2]. Additionally, Kroto and McKay also reported on the formation of quasi-icosahedral carbon nanoparticles with spiral shells [2-4]. This led to the discovery of a carbon allotrope exhibiting multi-layered curved graphene layers forming a quasi-spherical shape (particle size: 20-300 nm) and it was named carbon nano-onions (CNOs) owing to the nanoparticles' cross sectional resemblance of an onion [5-7].

Commonly, arc discharge and catalytic chemical vapor deposition are the most used methods to synthesize CNOs [8, 9]. Each synthetic method results in CNOs with different physical properties. CNOs formed by different methods can vary in their core type (i.e. metal core filled, hollow and solid), number of multi-layers (i.e. long or short range layering order), number of concentric shells, nano-particles shape (e.g. quasi-spherical, hexagonal or polyhedral) and size [8-14]. The layering of CNOs shells, graphitic nature, interlayer spacing and their structural morphology can be tuned by surface modification such as annealing and/or washing processes [14]. Moreover, the precursor (hydrocarbon source) used during synthesis also governs the type of CNOs that form [15].

Mohapatra *et al.*, reported a facile oil-wick open flame assisted synthetic method for producing solid quasi-spherical CNOs [16]. This is hydrocarbon(s) pyrolysis method which is catalyst free and it produces CNOs in grams scale. The method accommodates the use of various combustible hydrocarbon sources such as wood, wool, diesel, lycopene (from tomato) and petrol (gasoline) [16-18]. Additionally, the method is cost effective since it makes use of inexpensive hydrocarbon sources. Hence, in this study olive oil was selected as the hydrocarbon source since its general composition includes an assembly of lipids such as hydrocarbon and aliphatic alcohols [19-21].

Thus, it allows for the formation of CNOs exhibiting various oxygen species and/or oxygenated functional groups which are important for application purposes.

The formation of CNOs using the pyrolysis method is initiated by poly-aromatic hydrocarbons (PAHs) that react to form concentric fullerene-like shells, following a process similar to that of a snow accretion [22, 23]. However, hydrocarbons such as paraffin and vegetable oils usually produce CNOs with comparable particle sizes [24, 25].

Research on CNOs has been driven by the remarkable electrical, mechanical and physiochemical properties associated with the CNOs [26]. Due to these properties, the CNOs have been used in numerous applications such as catalysis, energy, sensing and storage devices [26-28]. Moreover, surface modifications of CNOs such as their polymer surface decoration finds application in areas such as solar cells, lithium-ion batteries, and biomedical materials in the form of CNOs composites [29]. The full potential and applicability of CNOs is also dependent on properties such as surface area as well as their solubility in both aqueous and organic solvents. Heteroatoms can also be introduced into the structural matrix of CNOs forming part of surface modifications which in turn affects both their chemical and physical properties [30-32]. Hence, like other carbon nanomaterials (e.g. carbon nano-tubes and fullerenes), CNOs have shown a great potential in chemical gas sensing device applications [33]. For example, Barbar and co-researchers recently reported on CNOs-polystyrene composite for detection of sulphur containing amino acids following the report by Mohapatra *et al.*, which was based on the enzymatic and non-enzymatic electrochemical glucose sensors fabricated using CNOs [34, 35].

Apart from the use of CNOs-polymer composites for chemical gas sensing, the sensing property of the CNOs can possibly be enhanced by its use in combination with various metal oxides [36]. Metal oxides are usually made from common metals such as manganese and zinc, are used in the fabrication of n-type semi-conducting sensors [37-40]. However, metal oxide-based sensors exhibit some limiting characteristics such as high cross-sensitivity, long-term signal drift, sensitivity to humidity and slow sensor response. Hence, nanomaterials such as chain-like CNOs (CLCNOs) can be mixed with metal oxides (e.g. MONRs) to improve the metal oxide-based sensor performance working at room temperature [40, 41].

The preparation of gas sensors for room temperature sensing is advantageous since it offers low power consumption and low ignition risk when detecting flammable or explosive analytes [41]. Thus, the use of CLCNOs will increase or promote the separation of charge carriers when blended or mixed with metal oxides (herein MONRs). This will offer cooperative or synergistic activity of

the CLCNOs-metal oxide composite material since the recombination of charge carriers will be reduced in the sensing device circuit allowing for increased migration of charge carriers [42]. A facile application of the nanomaterial in room temperature VOCs gas sensing systems will therefore be rendered by the use of CLCNOs since carbon nanoparticles have been previously used together with metal oxide and selected polymers to prepare sensors for detecting analytes such as 2-methylcyclopentanone, ethanol and methanol [36, 41, 43]. This study demonstrates for the first time the use of pristine CLCNOs and nitrogen doped CLCNOs-metal oxide-polymer composite in chemiresistive volatile organic chemical gas sensors (VOCGSs) as a gas sensing active material for detecting one of the treacherous VOC (i.e. acetone) at room temperature.

6.2. Experimental

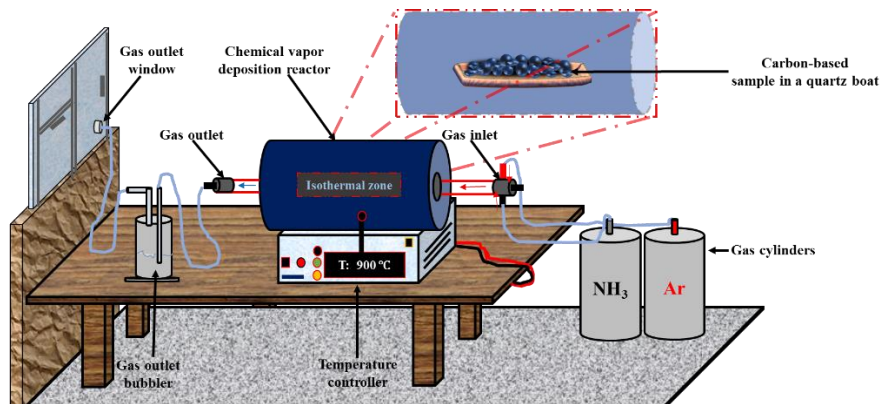
6.2.1. Starting materials

Olive oil (Hercules Company, Durban, South Africa) and a fibre glass wick (purchased from a local retailer) were used as received. A polished brass collecting plate (BCP, size: 140×140×1.5 mm) and a steel-tube stand (see **Scheme 5.1** in **Chapter 5**) were made in the University of the Witwatersrand Physical Sciences Workshop. Ammonia, argon and compressed air (NH₃, Ar, and Air) were purchased from Afrox, South Africa. Hexane, potassium permanganate (KMnO₄), manganese sulphate (MnSO₄·H₂O), acetone, polyvinylpyrrolidone (PVP) and dimethylformamide (DMF) were purchased from Sigma Aldrich/Merck and were used as received unless otherwise stated.

6.2.2. Synthesis of CLCNOs and metal oxide nanorods

About 15 mL of olive oil was transferred into a 50 mL glass container in which a fibre-glass wick was immersed and allowed to stand in the oil for 30 minutes [44, 45]. The glass container was placed beneath the BCP at the optimized distance of ~80 mm between the glass nozzle and the BCP as shown in **Scheme 5.1**. Finally, the distance between the luminous zone of the flame and the collection plate was maintained at ~20 mm. The wick was ignited to produce a flame in a controlled air environment. All other steps were followed as discussed in **Chapter 5** and the final product was labelled pristine CLCNOs (pCLCNOs). Thereafter, pCLCNOs were then doped with nitrogen using the ex-situ nitrogen doping process. The doping process of the pCLCNOs was

conducted using a chemical vapour deposition (CVD) method. The sample of pCLCNOs (150 mg) contained in a quartz boat was placed in a CVD reactor as shown in **Scheme 6.1**.



Scheme 6.1: Diagram showing the set-up used during the ex-situ doping process of CLCNOs.

Ammonia was passed through the sample in the presence of argon as the carrier gas at 1000 °C. The carrier gas (Ar) flow rate was kept constant at 100 sccm for all three experiments conducted, whereas the NH_3 flow rates were varied (100, 150 and 200 sccm) and the three samples collected were called a_1CLCNOs , $\text{a}_{1.5}\text{CLCNOs}$ and a_2CLCNOs respectively. Lastly, Manganese dioxide nanorods (MONRs) were synthesized using a method previously reported by Wang *et al.*, without any modification as discussed in **Section 5.2.3** [46].

6.2.3. Fabrication of the sensing devices

The initial step involved the preparation of a mixed materials solution (i.e. composite solution), using different CLCNOs (i.e. pCLCNOs, a_1CLCNOs , $\text{a}_{1.5}\text{CLCNOs}$ or a_2CLCNOs), MONRs, PVP and DMF. In this study, DMF was used as the preferred solvent due to its ability to disperse MONRs together with different CLCNOs (i.e. pristine and doped CLCNOs). PVP was used to stabilize the MONRs at room temperature. The preparation of different CLCNOs composites involved the use of 1:1:3 ratio for CLCNOs:MONRs:PVP which was added to 3 mL of DMF. The mixture was stirred for 12 h at room temperature followed by sonication for 1 h to obtain a homogeneous suspension of the composite. The clean inter-digitated electrodes (IDEs) were used in which different composite solutions were drop casted onto them by following a similar procedure discussed in **Section 5.2.4**. Herein, a micropipette was also used to drop cast 10 μL of

each composite solution onto different IDEs to give four different sensing devices. The resulting sensors were vacuum dried at 100 °C for 30 minutes, kept in a desiccator and labelled as pS, a₁S, a_{1.5}S and a₂S for sensors made from pCLCNOs, a₁CLCNOs, a_{1.5}CLCNOs and a₂CLCNOs respectively.

6.2.4. Fabrication and testing of the sensing devices

All sensors (pS, a₁S, a_{1.5}S and a₂S) were tested using the Agilent 4284A Precision LCR meter instrument. Selected frequencies (i.e. 1, 3, 6, 10 and 20 kHz) were used during the tests along with resistance measurements. The prepared sensors were tested using intervals of 1 µL per injection of acetone using a 2.4 L analysis chamber giving various concentrations of the analyte (i.e. acetone: 136, 271, 407, 543, 678 ppm), calculated using **Formula 2.1** in **Chapter 2** [47]. In a typical test, each analyte injection into the chamber was achieved by dropping 1 µL of acetone into a sealed chamber. The chamber was designed in a manner that dually allows for analyte injection and sensors exposure to different environments (see **Scheme 5.2** in **Chapter 5**). Tests were conducted in a sealed glove box environment in which the relative humidity (RH) was maintained at 27%. The RH below 30% was constantly monitored by using a constant flow of nitrogen at 300 sccm that was considered as a diluting purging gas used to limit and/or reduce high (i.e. RH: >30%) moisture contents that can greatly affect the analyte detection at 25 °C.

The resistance as a function of frequency measurements was conducted to select the best working frequency for each sensor using the chamber that was designed with a sweeping cover (see **Section 5.2.4**). This was done for a total of five injections each with 1 µL of the analyte injected into the chamber in which each sensor was exposed to the analyte for 150 seconds for every 1 µL of the analyte. Thus, any changes in frequency for each sensor were able to be observed considering the strength of the blank signal divided by the background noise of the blank signal over the same time, known as the signal-to-noise ratio (SNR), given by **Formula 2.3** [48]. The sensitivity (S_s) and the limit of detection (LoD) were calculated using **Formulae 2.4** and **2.5** respectively. Determinations followed the change in the sensor response per concentration unit of the analyte (i.e. the slope of a calibration curve) which is the sensitivity of a sensing device [49, 50].

Lastly, the lowest amount of analyte in the detection system that can be detected and that is significantly different from the blank, but not necessarily quantitated under stated experimental

conditions was estimated. This was achieved by using the LoD formula as given in **Section 2.1.2** [51, 52].

6.2.5. Characterization of the CLCNOs and MONRs

The morphology and characteristics of the CLCNOs produced were studied by using the scanning electron microscopy (SEM) technique and the FEI Nova Nanolab 600 FIB-SEM instrument was operated at 30 kV. The high magnification images of the CLCNOs were ascertained by transmission electron microscopy (TEM) using a Tecnai G2 30ST operating at 200 kV. The quality and structural properties of CLCNOs (supported on a silicon wafer (2 mg sample holder)) were investigated using a Jobin-Yvon T64000 Ultraviolet (UV) LabRam HR-micro Raman spectrometer with an Olympus BX41 microscope, that makes use of a liquid nitrogen cooled charge coupled device detector working at an excitation wavelength of 514.5 nm at room temperature. The thermal stability of CLCNOs (10 mg) was monitored using a Perkin Elmer 6000 thermogravimetric analyser. A Micromeritics Tristar 3000 surface area and porosity analyser was used to determine the surface area and pore volume of the CLCNOs (200 mg). The composition and/or surface elemental analysis of CLCNOs was achieved using three different techniques; (1) the Tescan Vega-3-LMU-SEM coupled with the energy dispersive spectroscopy (EDS) X-Max 80 detector (2) the LECO-932 carbon, hydrogen and nitrogen (CHN) analyser calibrated with a sulfamethazine as a standard, (3) the Physical Electronics Quantum 2000 X-ray photoelectron spectroscopy (XPS), that uses a monochromatic Al K α source operated at 1486.7 eV.

6.3. Results and discussion

6.3.1. Structural morphology analysis of the CLCNOs

The SEM micrograph revealed aggregation and/or conglomeration of quasi-spherical nanoparticles with particle sizes less than 100 nm (see **Figure 6.1(a)** and **6.2(a)**). The observed morphology from the SEM micrograph was similar to that of our previously reported work [53]. SEM micrographs of the doped CLCNOs (i.e. a_1 CLCNOs, $a_{1.5}$ CLCNOs and a_2 CLCNOs) showed similar conglomerated quasi-spherical morphology without structural deformations or distortions as shown in **Figure 6.2**.

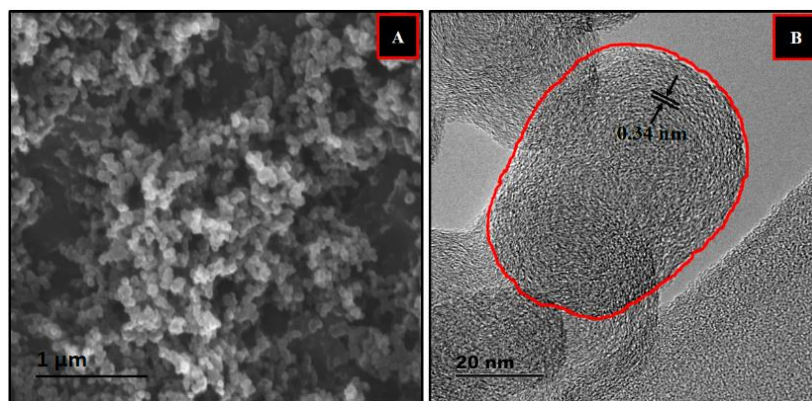


Figure 6.1: Microscopy micrographs of pristine CLCNOs; (a) SEM micrograph and (b) TEM micrograph.

Furthermore, the low magnification TEM micrographs revealed that CLCNOs exhibit dense or solid quasi-spherical shapes with particle sizes of ca. 55 ± 3 nm as shown in **Figure 6.3(b and c)** and **6.4** supporting the SEM data.

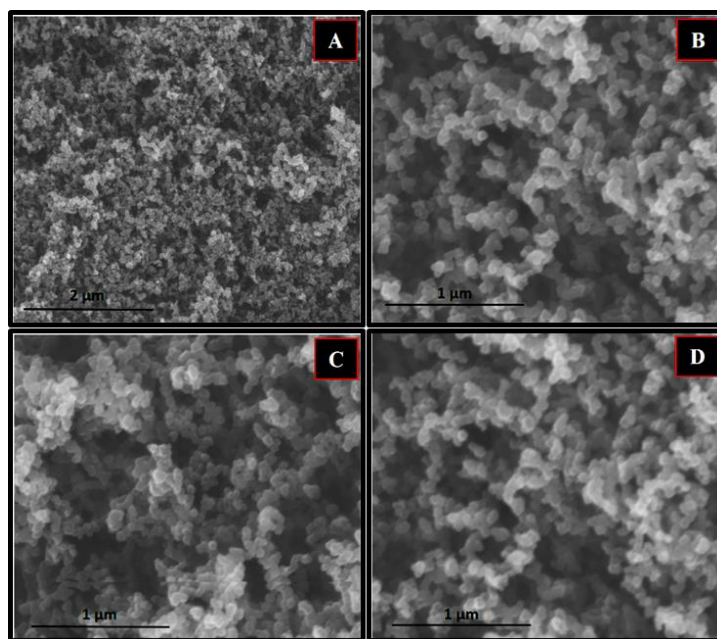


Figure 6.2: SEM micrographs of; (a) pristine CLCNOs, (b, c and d) N-doped CLCNOs for a_1 CLCNOs, $a_{1.5}$ CLCNOs and a_2 CLCNOs respectively.

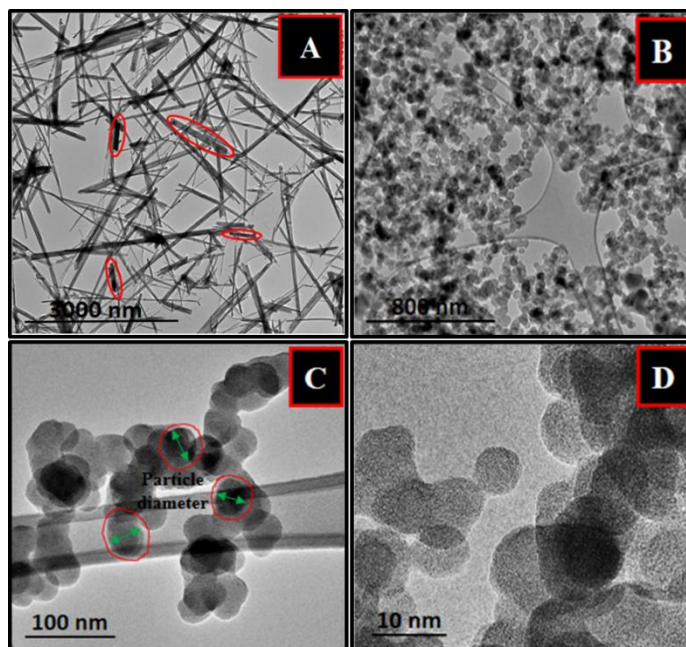


Figure 6.3: Low magnification TEM micrographs of; (a) manganese oxide nanoparticles, (b, c and d) pristine CLCNOs at different magnifications and/or regions.

It was also observed that the nanoparticles formed conglomerates which can be a result of Van der Waals forces leading to linkages of quasi-spherical nanoparticles that are comprised of closed cages (see the highlighted quasi-sphere in **Figure 6.1(b)**) similar to those obtained by Panda *et al.* [54]. This has revealed that the carbon nanoparticles produced are chain-like nanoparticles comprising multi-layered turbostratic shells. Moreover, the TEM results show concentric turbostratic shells of CLCNOs with radially continuous morphology of short-range ordered multiple concentric layers with the lattice fringe spacing of ca. 0.35 nm. The obtained lattice fringe spacing also indicated the presence of disordered graphitic carbon shells [16, 55, 56]. The formation of the short-ranged multi-layers can be attributed to the types of radicals that facilitate the growth process of individual particles during the flame pyrolysis process. Similar results were obtained in the work that was reported in the past years in which the growth process known as the “snow ball” growth process was discussed [53, 57, 58]. These results are comparable to those obtained by Mohapatra *et al.*, and Reddy *et al* [35, 59].

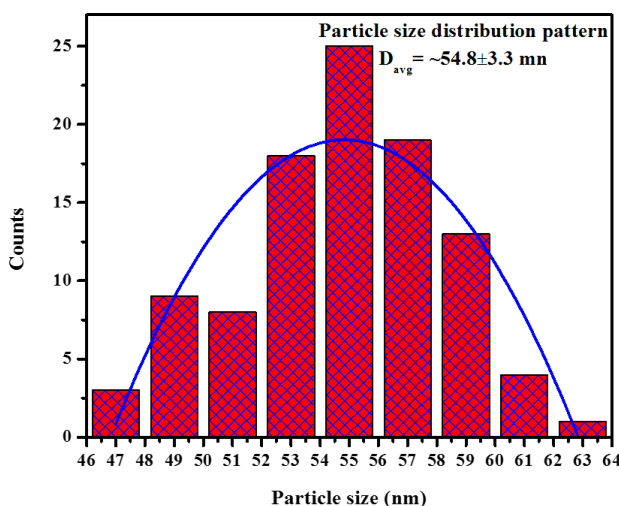


Figure 6.4: Particle size distribution based of the low magnification TEM micrographs obtained.

The nitrogen doped CLCNOs showed similar micrographs to those found for the pCLCNOs. The TEM micrographs shown in **Figure 6.3(b), (c) and (d)** indicates that CLCNOs material exhibit conglomerated, multi-centred concentric and short-range ordered nanoparticles. Notably, similar CLCNOs physical properties were still present following the doping process. This confirmed that the heat treatment during the doping process promoted further short-range ordering through nanoparticles healing and not the formation of new structural morphologies or growth of the nanoparticles.

6.3.2. Raman spectroscopic analysis of CLCNOs

A micro-Raman spectroscopy was used to investigate the structural properties of CLCNOs obtained. The position, intensity and breadth of both bands (i.e. D- and G-band) were used as the measure for determining the quality of the CLCNOs. It is evident that for all samples, that the D-band is positioned in the expected Raman region (i.e. between 1337 and 1346 cm^{-1}). This observation can be ascribed to the disorder induced by C–C vibrations corresponding to the disruption of the sp^2 hybridized carbon bonds. The suggested disruptions are due to the presence of dangling bonds, sp^3 bonding, C and H adatoms, intercalated C and H atoms, vacancies, as well as other carbon rings arising from structural conformations [9, 60]. Furthermore, the presence of this D-band further indicates the breathing mode of the six-fold aromatic rings in the carbon nanoparticles structural matrix and [9, 61]. Moreover, to quantify the degree of graphitization of CLCNOs, the ratio of the areas (fitted with Voigt line shapes using the Origin 8.5 inbuilt fitting

fixture) of the D-band to that of the G-band (I_D/I_G) was estimated. **Table 6.1** gives a summary of the Raman data obtained. The defects and/or disorder density ratio (I_D/I_G) are directly related to the extent of disorder in the form of sp^3 hybridized carbons and the presence of either longer or shorter graphitic fragments [60, 61]. It can also be seen that the I_D/I_G values of the pristine and doped CLCNOs were ca. > 0.5 , which further denotes a certain degree of graphitization (i.e. the presence of deformed graphitic carbon) depending on the sample.

The data in **Table 6.1** reveals that for all doped samples, there exists a down-shift (D-band) and an up-shift (G-band) with reference to the pristine sample respectively. This is an indication of the doped CLCNOs showing a curvature distortion since the curved carbon nanostructures such as carbon spheres, usually exhibit both the armchair and zig-zag edges at the graphitic boundaries [62-64]. Additionally, these shifts can be regarded to be proportional to the number of edges and/or in-plane terminations of either the pentagonal or hexagonal carbon network of the CLCNOs outer shells which can in turn change the sp^3 to sp^2 carbon fraction. This observation can be attributed to the healing effect(s) induced by the heat treatment during doping. Moreover, the results in **Table 6.1** also suggest that pCLCNOs, $a_{1.5}$ CLCNOs and a_2 CLCNOs exhibit higher quantity of sp^2 to sp^3 carbon content with a_1 CLCNOs having the lowest quantity of sp^2 to sp^3 but a higher sp^3 to sp^2 carbon content as its Raman spectrum shows a slightly higher D-band intensity than the G-band intensity. Thus, this is also supported by the intensities of the G-bands that are more intense than the D-bands for pCLCNOs, $a_{1.5}$ CLCNOs and a_2 CLCNOs respectively as shown in **Figure 6.5**.

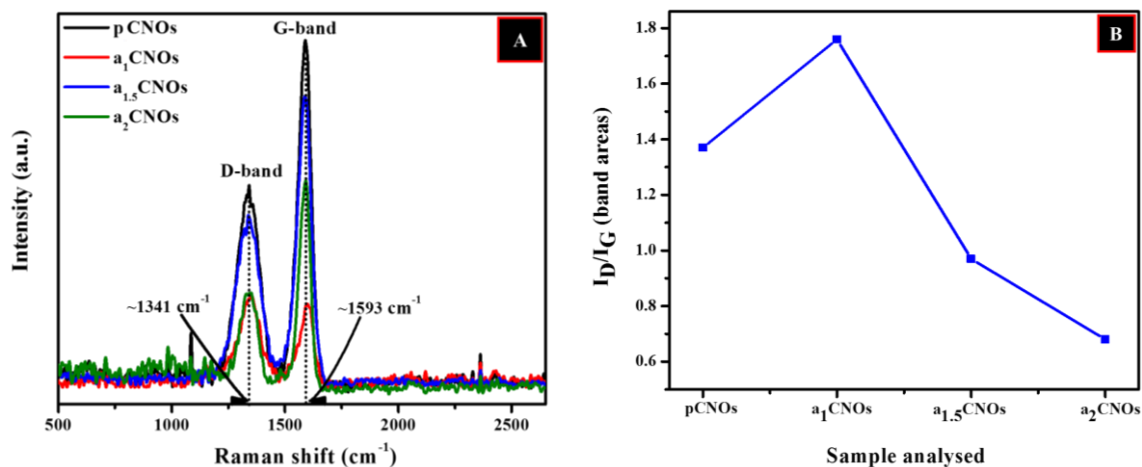


Figure 6.5: (a) Raman spectra of pCLCNOs and doped CLCNOs, (b) the I_D/I_G plot obtained using the D- and G-band areas for each sample.

In contrast, the D- and G-band FWHMs of the pCLCNOs are higher than those of the doped samples as shown by the deconvoluted peaks **Figure 6.6** and the results in **Table 6.1**. This indicates an increased amount of structural disorder that can be ascribed to the exposure of the in-plane terminations of either pentagonal or hexagonal carbon network of the CLCNOs outer shells as well as amorphous carbon impurities.

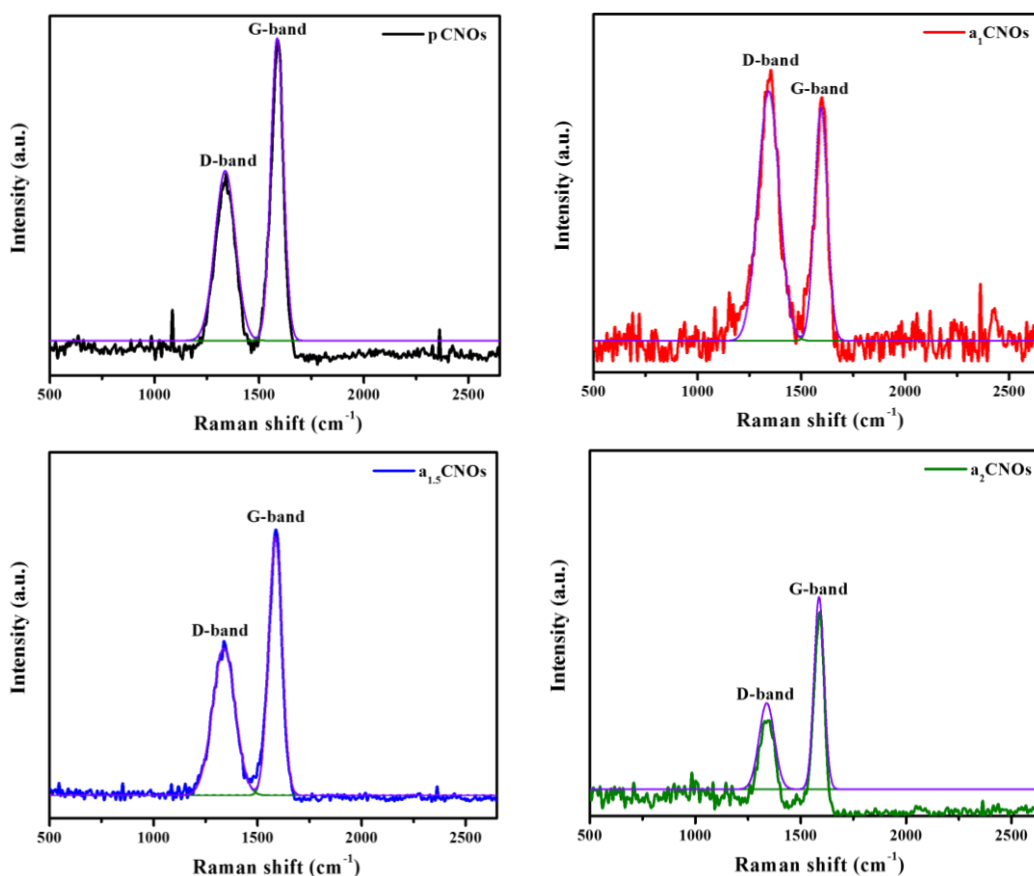


Figure 6.6: Raman spectra of pCLCNOs and doped CLCNOs.

The exposure of the in-plane terminations on the CLCNOs shells can be proposed to contribute to the amount of zig-zag edge defects, thereby increasing the sp^3 content within the curvatures of the shells of the pCLCNOs [65-67]. All doped CLCNOs samples showed Raman spectra with lower D- and G-band FWHM values as compared to that of the pristine CLCNOs sample, as shown in **Table 6.1**.

Table 6.1: Raman data of CLCNOs synthesized using flame pyrolysis.

Sample	Raman shift (cm ⁻¹)	Raman shift (cm ⁻¹)		FWHM	FWHM
	D-band	G-band	I _D /I _G	D-band	G-band
pCLCNOs	1345.9	1583.8	1.36	169.9	87.7
a₁CLCNOs	1342.7	1594.5	1.76	120.5	73.1
a_{1.5}CLCNOs	1337.7	1585.0	0.97	128.5	75.6
a₂CLCNOs	1339.0	1587.2	0.68	56.0	85.5

I_D: area of the D-band, *I_G*: area of the G-band, *I_D/I_G*: ratio of the areas (i.e. for D-band and G-band respectively).

This can be attributed to the addition of adatoms (i.e. N atoms) and/or removal of amorphous carbon impurities during the doping process. However, the defects and/or disorder density ratio (*I_D/I_G*) for all doped samples were estimated to be ca. 1.76, 0.97, and 0.68 for a₁CLCNOs, a_{1.5}CLCNOs and a₂CLCNOs respectively. This decreasing *I_D/I_G* trend suggests a remarkable reduction of the sp³ carbon content and the presence of incorporated adatoms (i.e. nitrogen heteroatoms) that usually contribute to the defective outer shell edges. Notably, the *I_D/I_G* ratio was also affected by the flow rate of NH₃. At a higher flow rate (i.e. 200 sccm), there are less adatoms formed due to an inadequate NH₃ residence time, which resulted in less N doping of the material. The higher *I_D/I_G* for a₁CLCNOs as compared to pCLCNOs (ca. *I_D/I_G*=1.36) suggests that the as-prepared CLCNOs were doped successfully with nitrogen heteroatoms using the lowest nitrogen source flow rate (i.e. 100 sccm) followed by a_{1.5}CLCNOs and a₂CLCNOs. However, both a_{1.5}CLCNOs and a₂CLCNOs had a lower *I_D/I_G* than the pCLCNOs due to a reduction of defects or disorder from the in-plane edges of either the pentagonal or hexagonal carbon networks of the CLCNOs outer shells.

6.3.3. Thermal stability of pristine and doped CLCNOs

The thermogravimetric analyses (TGA) and differential thermogravimetric analyses (DTA) data is in agreement with the Raman data. All CLCNOs samples decompose to completion (0% sample residue) by heat combustion process since the carbons residual mass remains at 0% following the completion of the TGA analysis as shown in **Figure 6.7(a)**. Thus, the obtained TGA profiles suggest rapid oxidative decomposition of the materials [68].

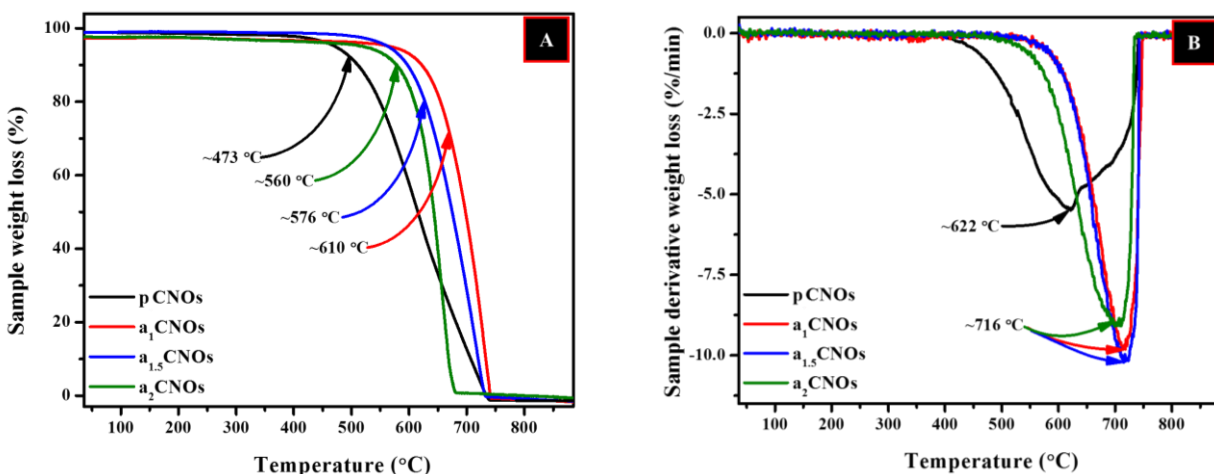


Figure 6.7: (a) Thermogravimetric analysis profiles of pristine and doped CLCNOs, (b) first-order derivative weight loss curves of pristine and doped CLCNOs.

The first-order derivative weight loss curves for all samples were established as shown in **Figure 6.7(b)**. The first-order derivative weight loss (FDW) curve for pCLCNOs exhibited a broader shape as compared to those of doped samples. The broader FDW curve for pCLCNOs showed that the decomposition of this material happens in two stages. The decomposition peak at ~ 622 °C suggests a first slow decomposition of the disordered graphitic outer shells whereas the shoulder observed around ~ 700 °C can be ascribed to the decomposition of the graphitic carbon core exhibited by pCLCNOs. The shoulder in the FDW curve of pCLCNOs at a higher temperature (around ~ 700 °C) signifies the presence of multiple centers or a core promoted by the conglomeration of nanoparticles as previously seen in the HMTEM micrographs (see **Figure 6.3(d)**).

It is also evident that the nitrogen doped CLCNOs homogenously decompose faster than the pCLCNOs since all the doped CLCNOs show narrower FDW curves. The doping process also increased the doped material thermal stability which suggests the doping process does not only introduces nitrogen adatoms but also strengthens the structural matrix of the turbostratic CLCNOs as shown in **Figure 6.7(b)** [69, 70]. On the other hand, the fitted Voigt line shapes shows that the broader peak for the pCLCNOs has a higher full width at half maximum (FWHM ca. 174.6) relative to those of the doped CLCNOs samples (FWHM ca. 76.9(a_1 CLCNOs), 78.0($a_{1.5}$ CLCNOs), and 94.7(a_2 CLCNOs)) indicating a slow decomposition of disordered pCLCNOs (see **Figure 6.8**). Furthermore, the narrow peaks with lower FWHM values can also be attributed to the structural rearrangements induced by heat treatment for all doped samples. Additionally, the FWHM value

of a_2 CLCNOs is higher than for both a_1 CLCNOs and $a_{1.5}$ CLCNOs which corresponds to the FWHM values of the Raman data obtained (Raman FWHM ca. 73.1 (a_1 CLCNOs) 75.6 ($a_{1.5}$ CLCNOs), and 85.5 (a_2 CLCNOs). This further suggests that the a_2 CLCNOs sample was poorly doped with nitrogen heteroatoms due to a higher dopant source flow rate (i.e. 200 sccm) [70].

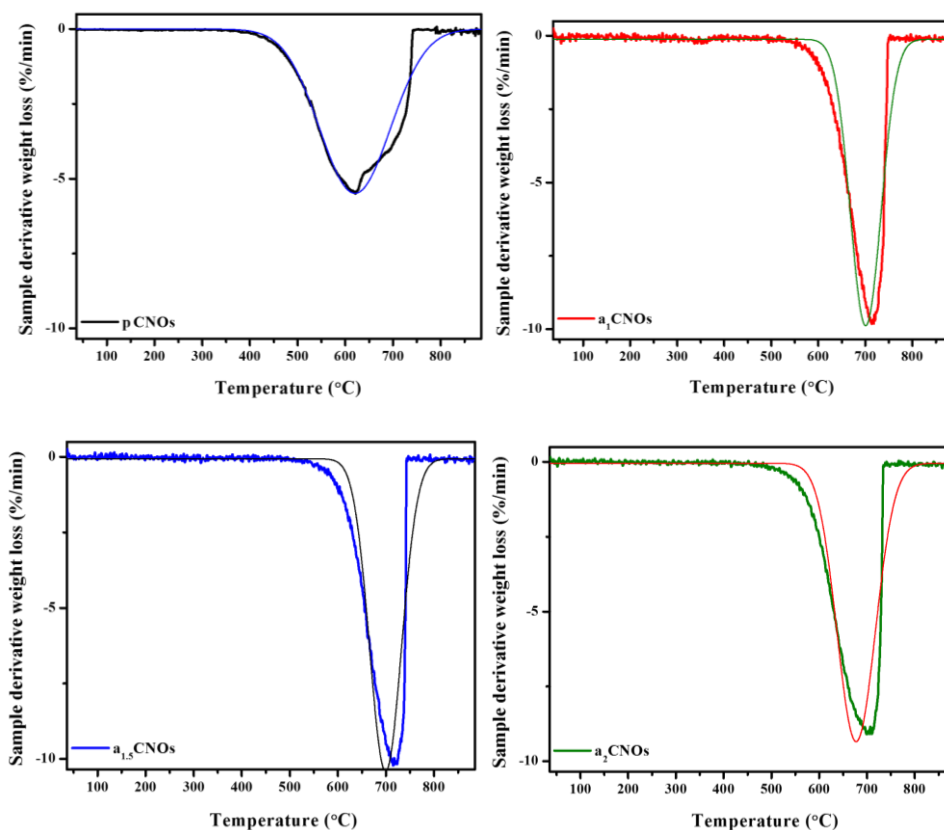


Figure 6.8: First-order derivative weight loss curves of pristine and doped CLCNOs.

In summary, the observed TGA profiles of all CLCNOs synthesized as well as their Raman and HMTEM data can be explained by considering the healing and growth processes involved during their synthesis. Therefore, the doping and heat treatment of the as-prepared CLCNOs can be thought of as promoting structural rearrangement and strength simultaneously leading to varied disordered graphitic CLCNOs with the different disorder or defect densities.

6.3.4. Elemental and surface area analysis of CLCNOs

The energy dispersive X-ray (EDX) spectra were analyzed and they showed that the as-synthesized CLCNOs are mainly composed of elemental carbon, oxygen, and nitrogen atoms on their structural surfaces (see **Figure 6.9** and **Table 6.2**).

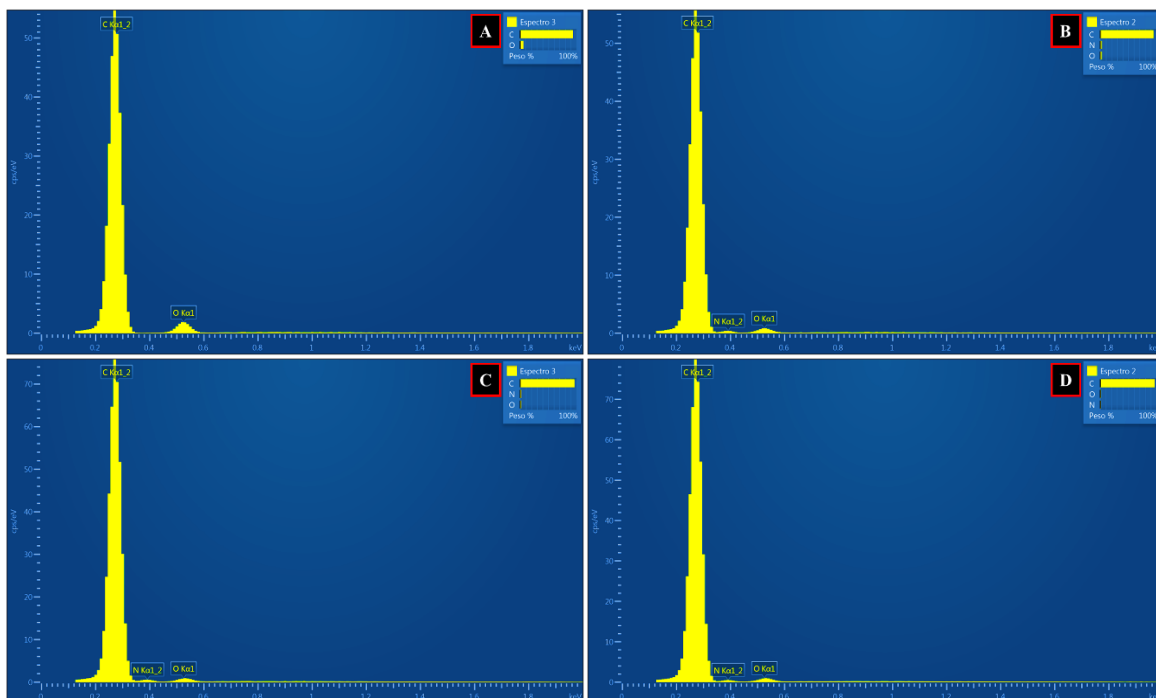


Figure 6.9: EDX spectra of (a) pristine CLCNOs, (b) a_1 CLCNOs, (c) $a_{1.5}$ CLCNOs, and (d) a_2 CLCNOs respectively.

Table 6.2: EDX elemental analysis data of all CLCNOs synthesized under different conditions.

Sample	Element		
	C (%)	N (%)	O (%)
pCLCNOs	95.34	0.00	4.66
a_1 CLCNOs	95.69	2.32	1.98
$a_{1.5}$ CLCNOs	97.12	1.73	1.15
a_2 CLCNOs	97.48	1.31	1.21

Notably, the carbon peaks are not only as the result of the carbon based samples but also from the SEM carbon tape on which the sample was deposited which is the component that cannot be

avoided when using SEM-energy dispersive spectroscopy technique. Adding to the EDX results, the CHN results shown in **Table 6.3** reveals that all samples are predominantly made of carbon with the hydrogen contents less than 3%. A decrease in nitrogen content for doped samples was observed as the flow rate of NH_3 increased. The results in **Table 6.3** show that a_1CLCNOs (N: 3.34%) has a higher nitrogen content when compared to $\text{a}_{1.5}\text{CLCNOs}$ (N: 3.28%) and a_2CLCNOs (N: 2.89%). These results signifies that the use of higher NH_3 flow rate when doping CLCNOs has discouraged the introduction of nitrogen heteroatoms. Moreover, the doping process can introduce different types of nitrogen species in the CLCNOs structural matrix as suggested by Dias *et al* [71]. Hence, for most carbonaceous nanoparticles, there exist possibilities for the formation of graphitic, pyridinic, or pyrrolic nitrogen sites as well as lactam, pyridinic oxide and/or amine type of nitrogen attachments on the surfaces of CLCNOs [72, 73].

Table 6.3: CHN data for the different CLCNOs synthesized by varied processes.

Sample	Element		
	C (%)	H (%)	N (%)
pCLCNOs	90.42	7.54	0.00
a_1CLCNOs	89.11	0.54	3.34
$\text{a}_{1.5}\text{CLCNOs}$	82.73	2.23	3.28
a_2CLCNOs	70.43	1.21	2.89

The XPS data (**Figure 6.10(a)**) reveals that the pristine CLCNOs exhibit C and O atoms in the structural matrix which can form groups such as the carboxylic acid groups [74, 75].

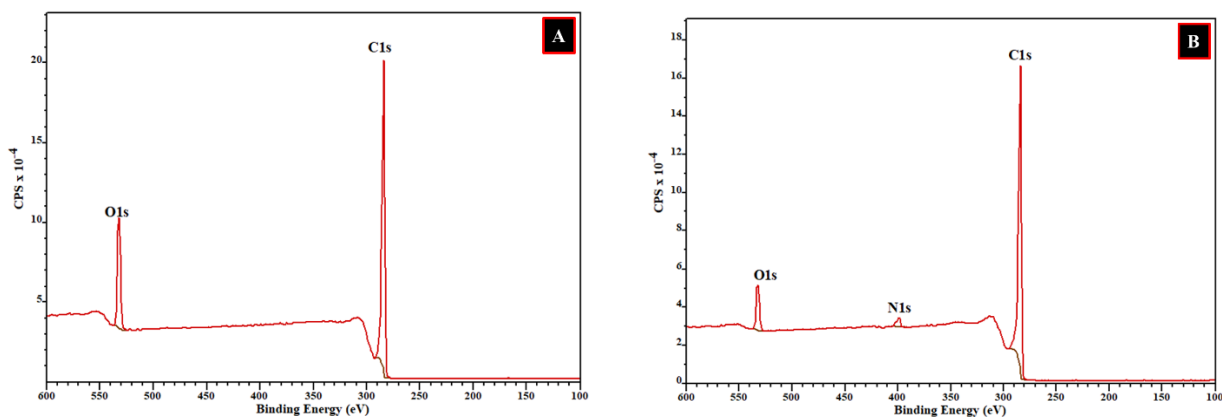


Figure 6.10: XPS survey scan of (a) pCLCNOs, (b) a_1CLCNOs .

The XPS data for a₁CLCNOs also revealed that the sample exhibited various carbon and oxygen atom arrangements along with different N bonding patterns (graphitic, pyridinic, or pyrrolic nitrogen) that exist on the a₁CLCNOs surfaces (see **Figure 6.10(b)** and **6.11**) [72, 75]. The deconvolution of the C1s peak gave rise to different C atom types and the signals obtained comprises of C atoms that are hybridized differently (i.e. sp² and sp³, see **Figure 4(a)**) [76, 77]. Additionally, the deconvolution of the N1s peak revealed significant information about the different types of nitrogen that are associated with the a₁CLCNOs. It is evident from Figure 4(b), that a₁CLCNOs exhibit four different types of N groups and the corresponding peaks for pyridinic-N, pyrrolic-N, graphitic-N, and oxygenated pyridinic-N (i.e. NO_x) were positioned at 397.71 eV, 398.48 eV, 400.15 eV, and 402.83 eV respectively (also see **Figure 4(d)**) [72, 78]. This indicates a wide range of N type species with different average percentage concentrations of the N atoms present viz. 23.64%, 37.59%, 21.32%, and 17.44% for pyridinic-N, pyrrolic-N, graphitic-N, and oxygenated pyridinic-N respectively. Thus, the pyrrolic-N configuration dominated the sample that signifies the formation of a carbonaceous sample that is capable of donating charge carriers [79, 80].

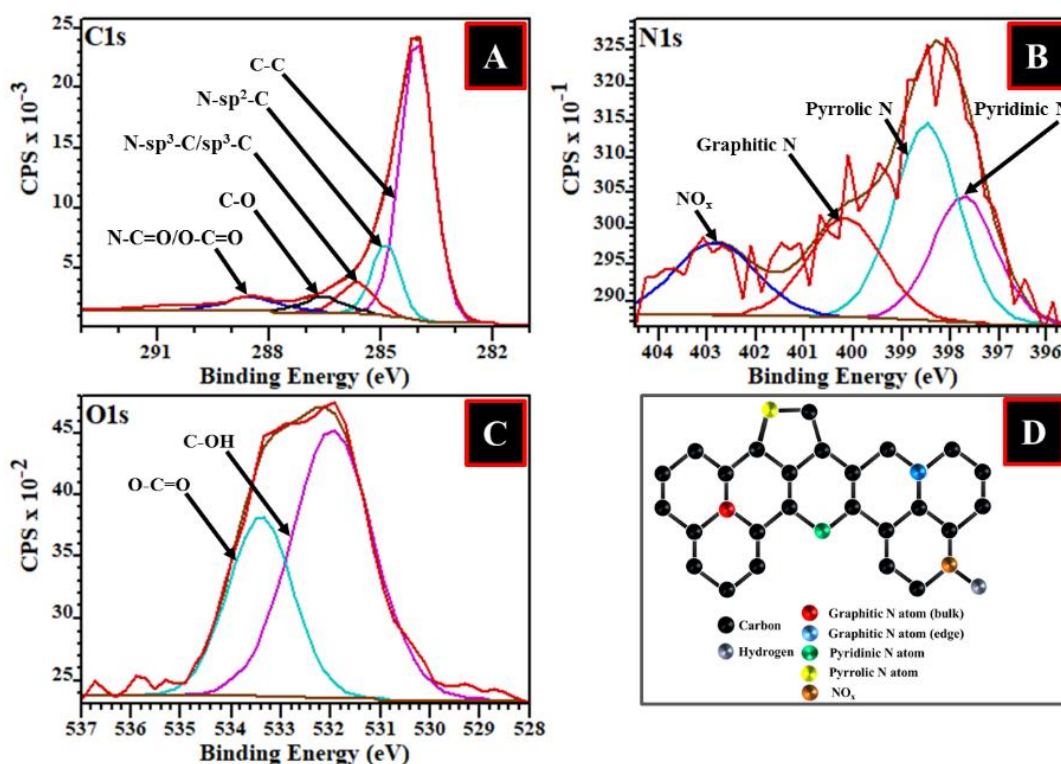


Figure 6.11: XPS survey scan of the deconvoluted spectra of a₁CLCNOs; (a) C1s, (b) N1s, (c) O1s, and the (d) proposed N configurations exhibited by a₁CLCNOs.

Lastly, the O1s peak was also deconvoluted as shown in **Figure 6.11(c)**, and it can be confirmed that the a₁CLCNOs sample also contained oxygenated carbon atoms with different bonding configurations [7, 81]. Hence, the nanoparticles produced exhibited different oxygen species on their surfaces [81, 82].

The surface properties (i.e. the surface areas (SA) and pore sizes (PS)) of all CLCNOs were investigated using the BET surface characterization technique. The surface area of pCLCNOs (69 m²/g) was less than that of the doped samples and showed a decreasing pattern with increasing flow rate of NH₃ as; a₁CLCNOs (206 m²/g), a_{1.5}CLCNOs (191 m²/g) and a₂CLCNOs (188 m²/g) (see **Figure 6.12**). The increased content of adatoms improved the surface area of the as-synthesized CLCNOs, which was supported by the heat treatment that promoted the reduction of amorphous carbonaceous mass upon doping. Hence, this suggests the continuous accretion of pCLCNOs particles forming multiple nucleation centres supported by the amorphous carbonaceous mass before the doping process.

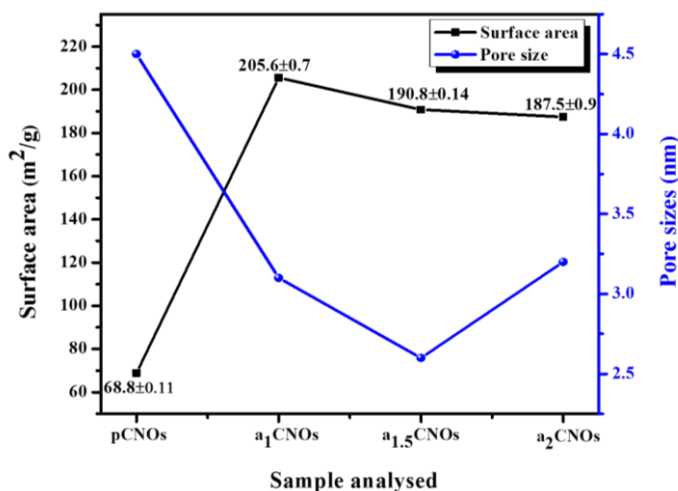


Figure 6.12: Plot showing changes in the CLCNOs pore sizes and surface area.

Furthermore, the pore sizes plot in **Figure 6.12** shows that all CLCNOs samples exhibit inter- and intra-particle pores and this could suggest that the calculated defect density using the Raman data could be largely contributed by these inter- and intra-particle pores. The pore sizes are different for all CLCNOs samples which can be due to the possible formation of inter- and intra-particle pores on the outer shells of CLCNOs depending on the conformation of the nanoparticles. In summary, the BET results indicate that the surface properties of the CLCNOs (i.e. the surface area

and pore size) are greatly influenced by the synthesis parameters (e.g. heat treatment and dopant source flow rate) which affect the curvature, shape and direct contact area (aggregation or agglomeration) of carbon nanoparticles.

6.3.5. Electrochemical tests: Static characteristic measurements of the sensing devices for detecting VOCGs based on different CLCNOs

Four different sensors (i.e. pS, a₁S, a_{1.5}S and a₂S) were fabricated and tested. The signal to noise ratio (SNR) was determined using **Formula 2.3** discussed in **Section 2.1.2** in which different working frequencies were used (i.e. 1 kHz, 3 kHz, 6 kHz, 10 kHz and 20 kHz). Most of the sensing devices showed the highest SNR values exists at 10 kHz relative to the frequency working range (see **Figure 6.13**). Hence, 10 kHz was selected as the optimal working frequency for all the sensors. Moreover, the use of this frequency is preferred because it allows for facile fabrication of sensing systems that use lower electrical power [83].

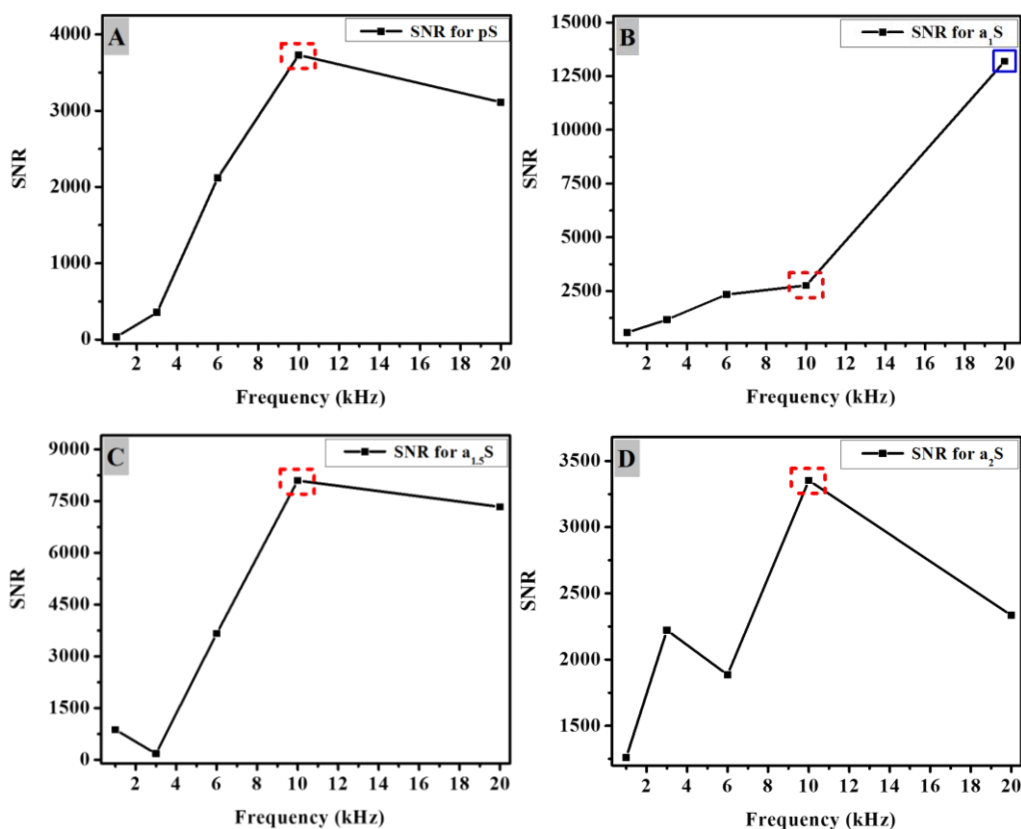


Figure 6.13: SNR plots representing different sensors (i.e. pS, a₁S, a_{1.5}S and a₂S) response for; (a) pS, (b) a₁S, (c) a_{1.5}S and (d) a₂S respectively.

A similar response towards acetone was shown by the decrease in resistance with an increase in acetone concentration (0 ppm - 678 ppm) for all sensors as shown in **Figure 6.14**. The differences in the shape of the baseline (i.e. resistance (R) versus frequency (f) curves at 0 ppm) are as the result of potential kinetically controlled states (see **Figure 6.14**). This also includes the adsorption processes that involves chemisorption and/or physisorption for every sensing device. Thus, it can also be attributed to the dispersion and film thickness of the active sensing material. The sensors' response ($\Delta R/R_0$) as a function of frequency plots revealed that the shape of the baselines for the blank measurements varied with different sensors as shown in **Figure 6.15**.

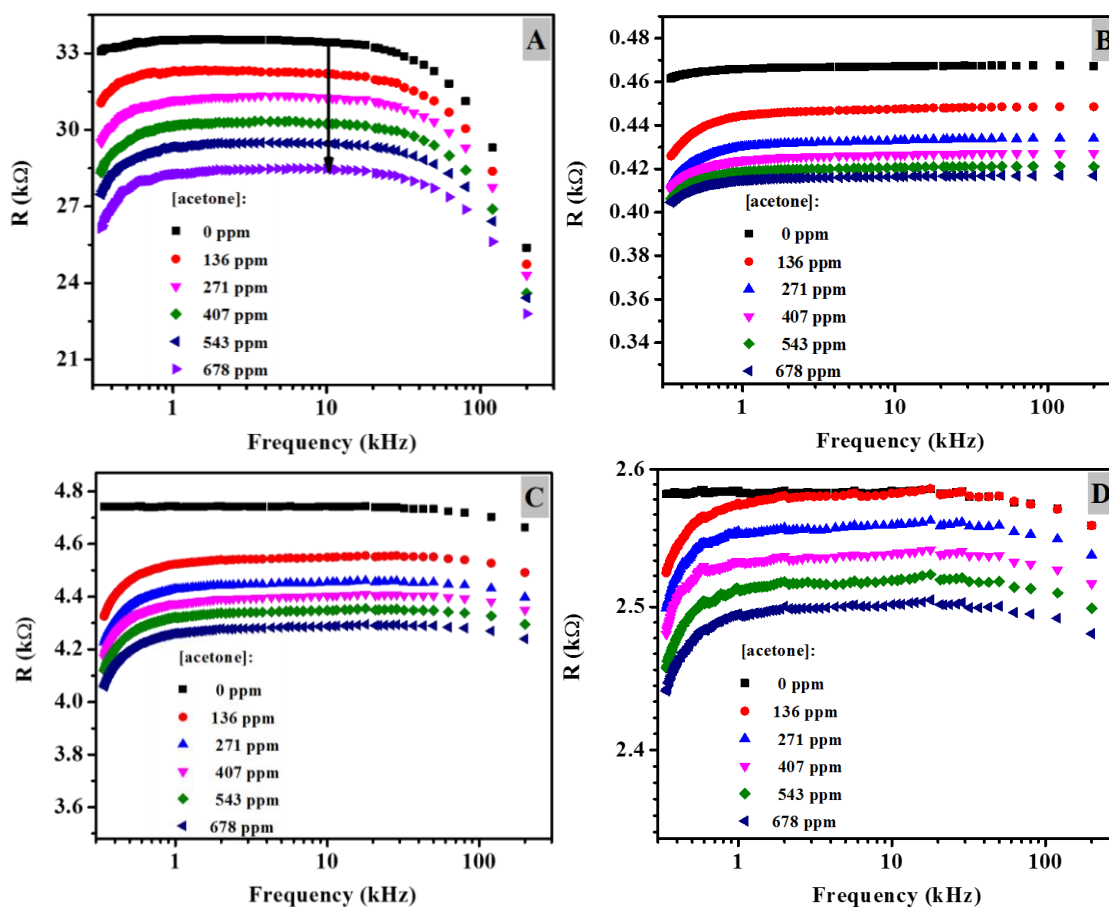


Figure 6.14: Plot of resistance (R in $k\Omega$) as a function of frequency for (a) pS, (b) a₁S, (c) a_{1.5}S, and (d) a₂S for varied acetone concentrations.

These observations suggest that the adsorption of the acetone molecules on a CLCNs-based sensing material selectively depends on the dipole-moment, polarity, porosity, as well as vapor pressure of the carbon surface used in the sensing composite [84, 85]. Acetone is one of the VOCs

that is regarded as a polar aprotic analyte which means it is incapable of donating protons in hydrogen bonding interactions [86]. Polar and volatile analytes usually interact with functional groups and/or active sensing sites on the sensing material surface more than their nonpolar counterparts. Thus, acetone can also facilitates its molecular interaction with the carbonaceous sensing material. Hence, in this study it is regarded as a reducing gas or electron donor based on its molecular properties. This was indicated by the decrease in resistance (i.e. increased conductivity) during its detection [87, 88].

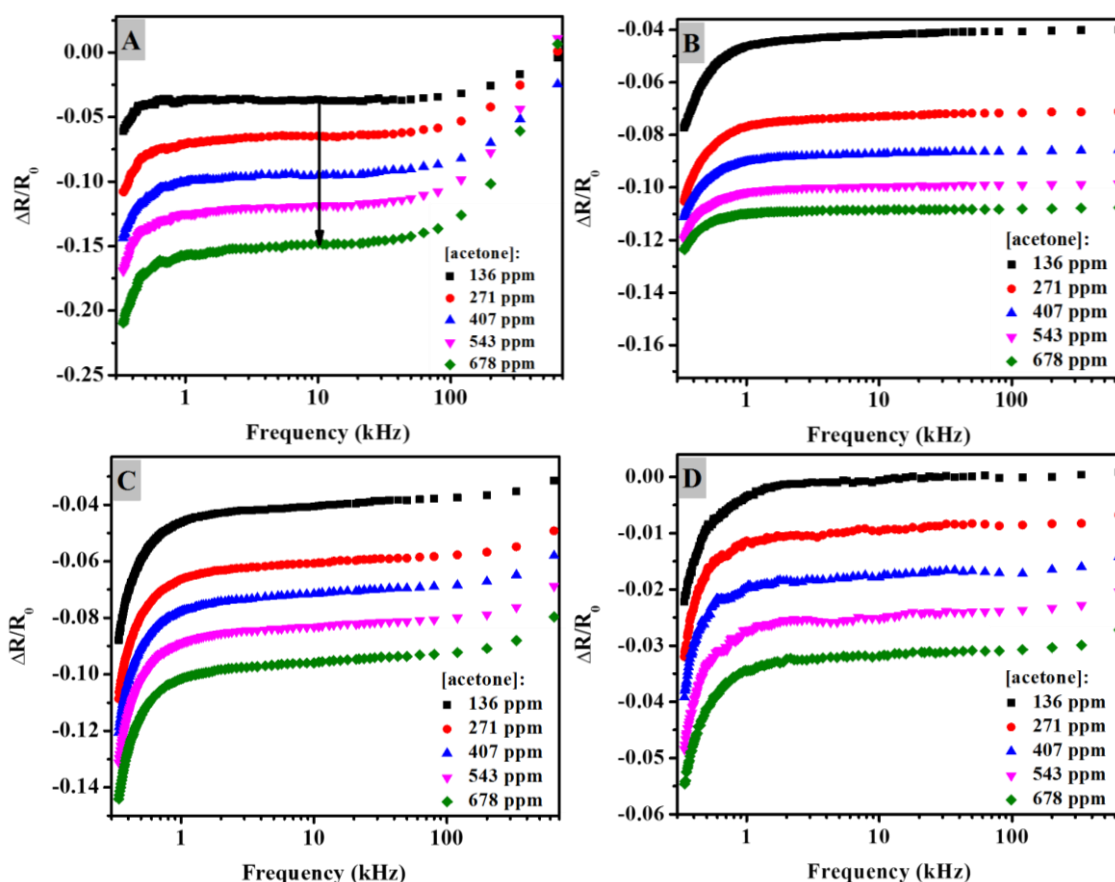


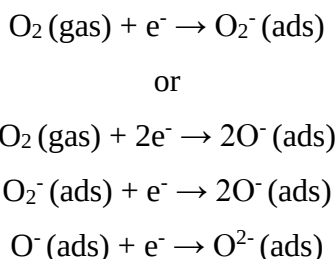
Figure 6.15: Graphs indicating the sensors response ($\Delta R/R_0$) towards varied acetone concentrations as a function of frequency for; (a) pS, (b) a_1S , (c) $a_{1.5}S$, and (d) a_2S .

Consequently, the presence of carbon embedded or supported manganese oxide nanoparticles in the sensing composites provides the n-type semiconducting properties with electrons as major charge carriers in the system containing a reducing gas. Notably, most metal oxides (e.g. MONRs) indicate the existence of O_2^- (superoxide) which rarely exists in carbonaceous materials such as in

CLCNOs [89]. Since CLCNOs can exhibit all other types of oxygen species except for the superoxide species, this means that the metal oxide can provide this important species for better gas sensing properties when a composite of the two materials (i.e. CLCNOs and MONRs) is used [90].

Considering that all acetone sensing tests were conducted in an environment in which the relative humidity (RH) was maintained at 27%, there existed oxygen carrying species such as the water (H₂O) molecules in the sensing system. The major charge carriers can be from different oxygen species that are responsible for establishing the charge equilibria on the carbon distributed metal oxide surface. Different oxygen species on the surface of carbon distributed metal oxide sensing material can be generated by the adsorbed oxygen molecules from the air exposure during the sensing device preparation. These oxygen species can either be electrophilic or nucleophilic in which those that are electrophilic (i.e. O⁻ (oxide), O₂⁻ (superoxide), and O₂²⁻ (peroxide)), exhibit electron deficiency with a tendency to attack any available electron-rich regions of hydrocarbon molecules such as C=C bonds [91]. Alternatively, the nucleophilic type of oxygen species, such as O²⁻ (oxo), are usually involved in C-H bond cleavage (either homolytic or heterolytic) during oxidative dehydrogenation. However, in some instances, some oxygen species gradually change from electrophilic to nucleophilic by electron enrichment during the surface reactions, from O₂⁻ (superoxide) to the O²⁻ (oxo) state [92].

The existence of oxygen species such as O²⁻ on the sensing material can promote the formation of a surface inversion layer resulting in a specific sensing response depending on the properties of the sensing material. This can occur when the oxygen species such as O₂⁻ dissociates after capturing an additional electron from a donor to form another oxygen species as described in the reaction equations below [93]:-

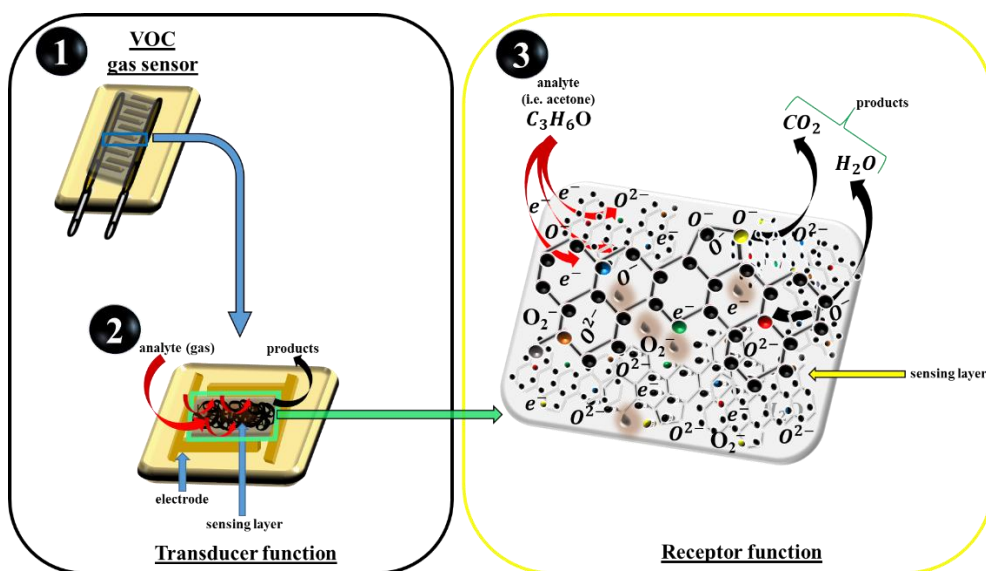


These important ionized species can further promote identification and total oxidation of acetone to form carbon dioxide and water in the receptor function of the sensor as depicted in **Scheme 6.2**

[94]. Thus, it can be suggested that the oxidation of acetone molecules at the surface of the sensing materials follows the reaction mechanism below [95]:-



Furthermore, the change in resistance is also attributed to a relatively stronger charge transfer interaction (i.e. chemisorption) as opposed to a weaker dipole or Van der Waals forces (i.e. physisorption) [96, 97].



Scheme 6.2: Proposed acetone sensing mechanism for CLCNOs-based composite.

Semiconducting metal oxides commonly show the abundant adsorption of oxygen species with negative charge forming electron-depletion layers (EDLs) near the surfaces of n-type metal oxide semiconductors [98]. Hence, the introduction of negative charges by acetone occurs on the sensing material environment such that its molecules can greatly interact with the negatively charged oxygen species on the surface of CLCNOs distributed and/or embedded metal oxides (MONRs) nanoparticles [99]. The trapped electrons in the PVP/CLCNOs/MONRs composite sites are therefore injected into the EDL leading to the electron concentration increase and ultimately the decrease in resistance of the sensors [98, 100].

In summary, the composites used in this study reveal the synergistic effects between all materials used in the mixture (i.e. PVP, CLCNOs and MONRs). The obtained results suggest that the response of the sensors is greatly influenced by simultaneous surface interactions of acetone gas molecules with different CLCNOs and/or MONRs nanoparticles that form the sensing composite. However, this depends on the availability or exposure of active adsorption sites which can also be influenced by the dispersion and film thickness of the active sensing material.

The resistance and response results obtained revealed an n-type behavior for all sensors as shown by a decrease in resistance with increasing acetone concentrations. This observation was then followed by determinations of the sensitivity of the sensors (S) under the decreasing resistance and SNR conditions (i.e. at 10 kHz for varied acetone concentrations (ppm) respectively). The change in each sensor's response per concentration unit of the analyte was determined as the sensor's sensitivity (S) using the slope of the calibration curve. The results in **Figure 6.16** and **Table 6.4** reveals that the pS sensor ($S: 2 \times 10^{-4}$) is the most sensitive toward the detection of acetone. The observed decreasing order of sensitivities is pS ($S: 2.0 \times 10^{-4} \text{ ppm}^{-1}$) > a₁S ($S: 1.2 \times 10^{-4} \text{ ppm}^{-1}$) > a_{1.5}S ($S: 9.5 \times 10^{-5} \text{ ppm}^{-1}$) > a₂S ($S: 5.7 \times 10^{-5} \text{ ppm}^{-1}$) further indicates that all sensors fabricated using nitrogen doped CLCNOs composites exhibit lower sensitivities towards acetone. However, a decreasing order of sensitivities was maintained by sensors fabricated using nitrogen doped CLCNOs composites since a₁S ($1.2 \times 10^{-4} \text{ ppm}^{-1}$) > a_{1.5}S ($9.5 \times 10^{-5} \text{ ppm}^{-1}$) > a₂S ($5.7 \times 10^{-5} \text{ ppm}^{-1}$). This observation can be due to the presence of the carbonyl groups (C=O) in the molecular structure of acetone molecules. These organic groups creates an electron donating effect on the CLCNOs-MONRs based surface that is rich with oxygenated groups leading to a better sensitivity of pS as compared to sensors based on nitrogen doped CLCNOs. Thus, the presence of adatoms, oxygenated groups and/or amorphous carbon impurities in the pCLCNOs sample contributed to the higher sensitivity obtained for pS sensor. This is attributed to the availability of multi-active attachment sites on the pCLCNOs based composite layer for the attachment of acetone molecules. Moreover, a₁S was the highly sensitive sensor as compared to a_{1.5}S and a₂S due to a₁CLCNOs being the most favored sample during the doping process (i.e. a₁CLCNOs are highly defective with higher N content (electron-rich)) [10].

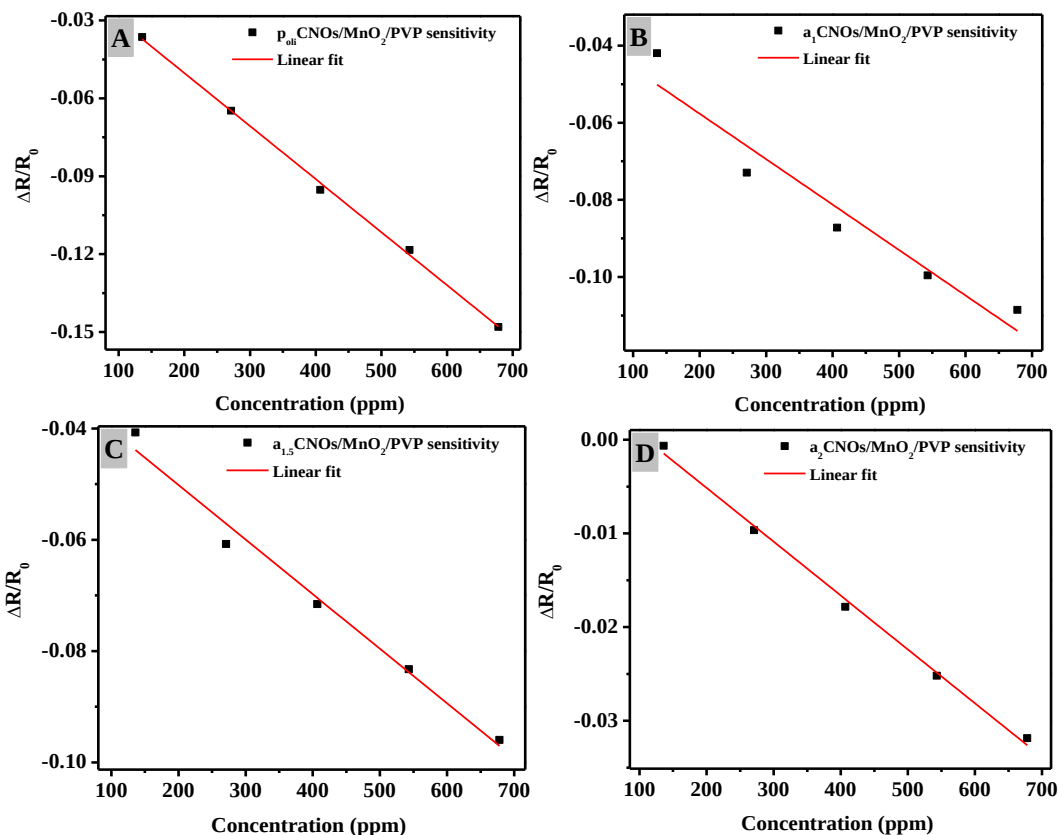


Figure 6.16: Sensor's response ($\Delta R/R_0$) operating at 10 kHz as a function of varied acetone concentrations with the slopes of the calibration curves for; (a) pS, (b) a₁S, (b) a_{1.5}S, and (d) a₂S respectively.

Additionally, a₁S was the second most sensitive sensor following pS because the predominantly doped a₁CLCNs used for a₁S exhibited nitrogen defective sites that hindered the attachment of acetone molecules. However, the nitrogen defective sites exhibited by a₁CLCNs alternatively promoted charge transport through proton hopping within the PVP/a₁CLCNs/MONRs based composite. Hence, the decrease in charge carrier resistance on the surface of the active nanoparticles was observed. The lowest amount of acetone in the detection system that can be detected and that is significantly different from the blank was determined using the LoD formula (see **Section 2.1.2**). As shown in **Figure 6.17**, the LoD results for all sensors indicates that the sensor with the lowest LoD is a_{1.5}S (LoD: 1.2 ppm) but it is the third most sensitive sensor towards acetone.

Furthermore, the summary in **Table 6.4** also reveals that the most sensitive sensor (i.e. pS) is the device with the second lowest LoD. Notably, the LoD (2.9 ppm) of pS is lower than that of the sensor fabricated using nitrogen doped hollow carbon spheres (N-HCS) reported by Mutuma *et*

al., (LoD: 83 ppm) [101]. Moreover, Mutuma *et al.* reported a lower sensitivity ($S: 1.5 \times 10^{-4} \text{ ppm}^{-1}$) than that shown by pS ($S: 2.0 \times 10^{-4} \text{ ppm}^{-1}$). This can be associated with the presence of different oxygenated groups on the pCLCNOs surface edges that are additionally contributing to the type of oxygen species exhibited by the active composite in the sensing device (i.e. pS sensor). However, the sensitivity reported by Mutuma *et al.*, was higher than the sensitivities of all sensors prepared using doped samples [101]. This can be attributed to the inactive nitrogen-induced defects in the doped CLCNOs surface that unfavorably allowed for the interaction of the nitrogen-containing groups with acetone molecules depending on the type of nitrogen adatoms present on the CLCNOs surfaces.

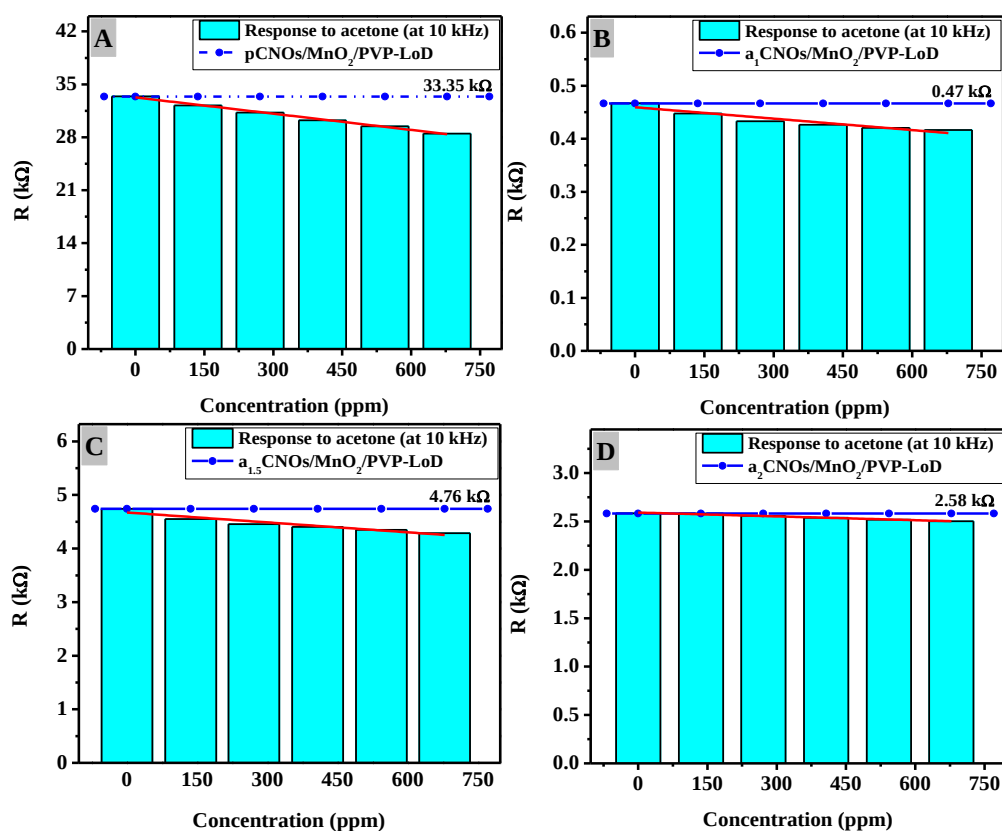


Figure 6.17: Resistance at 10 kHz as a function of analyte (acetone) concentration, the blue horizontal line indicates the estimated LoD resistance of the corresponding sensors respectively.

Table 6.4. Summarizes the determined sensitivities and limit of detection concentration (LoD) for different sensors based on CLCNOs composites as compared to other related studies conducted under room temperature conditions.

Analyte	Concentration (ppm)	Material(s)	LoD (ppm)	Sensitivity (ppm ⁻¹)	Ref.
Acetone	0-678	PVP/pCLCNOs/MONRs	2.9	2.0×10 ⁻⁴	This work
Acetone	0-678	PVP/a ₁ CLCNOs/MONRs	3.6	1.2×10 ⁻⁴	This work
Acetone	0-678	PVP/a _{1.5} CLCNOs/MONRs	1.2	9.5×10 ⁻⁵	This work
Acetone	0-678	PVP/a ₂ CLCNOs/MONRs	140	5.7×10 ⁻⁵	This work
Acetone	0–489	N-HCSs-50	83	1.5×10 ⁻⁴	101
Acetone	NR	MWCNTs/Fe	NR	0.8×10 ⁻²	102
Acetone	NR	HKUST-1 MOF {(Cu ₃ (BTC) ₂ (H ₂ O))}	50	NR	103

NR: Not reported, LoD: Limit of Detection.

The use of the various carbon and metal oxide composite in this study offers different sensing ability towards acetone due to the rapid adsorption of the reducing gas. Hence, the significance of this study is the finding of low LoD and sensitivity values recorded for acetone using pristine CLCNOs (i.e. pCLCNOs) as compared to other reports in the literature [101-104]. Despite the low sensitivity shown by some of the sensors (e.g. a₂S) towards acetone, the ability to detect it at lower concentrations by all sensors is also a significant finding. Furthermore, the results reveals that the controlled temperature and relative humidity gives a great potential to improve the chemical sensing properties of carbon and metal oxide nanoparticles based composites. These results also suggest future modification of carbon composites based chemical sensors. Thus, this study reports the fundamental sensing properties of olive oil derived pristine and doped CLCNOs towards acetone gas molecules. Moreover, it also gives indications that the predominance of nitrogen adatoms plays a significant role in the detection process of acetone by also involving a specific type of nitrogen (e.g. pyrrolic-N) present on the surfaces of CLCNOs nanoparticles.

6.4. Conclusions

A facile synthesis of quasi-spherical CLCNOs with particle sizes of ca. 55 nm was successfully achieved using the olive oil flame pyrolysis process. Upon nitrogen doping of CLCNOs, the defect density induced in the CLCNOs structural matrix was decreased with increasing dopant source flow rate used in the CVD reactor. The presence of CLCNOs structural defects and/or disorder was confirmed by the variable breadth of the first-order derivative peak (DTA, FWHM data) as well as the Raman band area I_D/I_G ratios. The surface areas of all the ex-situ doped CLCNOs were $> 150 \text{ m}^2/\text{g}$ and directly proportional to the nitrogen content. The successful doping of CLCNOs was confirmed by the CHN data which revealed the presence of nitrogen for all doped samples (between 2 and 4% N content). These results were further supported by the EDX and XPS data in which different oxygen species were also identified to be present in various CLCNOs prepared along with the dominance of the pyrrolic-N configuration. The pristine and doped CLCNOs showed a positive response towards the detection of acetone which was promoted by the presence of different hetero-atomic species exhibited by CLCNOs.

Significantly, the pS sensor exhibited higher sensitivity towards acetone indicating that the role of ex-situ nitrogen doping process only promoted the use of highly durable CLCNOs with decreased surface active sites leading to poor analyte-active sensing surface interactions as revealed by Raman and TGA results. The obtained data indicated that the physicochemical properties of the materials used to form the composites (i.e. PVP, CLCNOs and MONRs) influence how the fabricated device responds towards the detection of acetone at room temperature. The LoDs and sensitivities obtained revealed a positive response of the prepared sensors towards acetone. However, the response was only observed when the three materials (i.e. PVP, CLCNOs and MONRs) were used to form the composite. Moreover, the a_1S detector showed better sensitivity towards acetone as compared to other sensors fabricated using doped CLCNOs (i.e. $a_{1.5}S$ and a_2S) which also suggests the use of nitrogen doped carbon nanoparticles for detection of acetone. Thus, there is great potential to improve the chemical sensing properties using different composites of carbon nanoparticles, such as CLCNOs, and various metal oxide nanoparticles.

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CHAPTER 7

Application of in-situ doped carbon nano-onions in chemiresistive gas sensors for detecting acetone, ethanol and toluene at room temperature

7.1. Introduction

Recently, there is a rapid increase in the development of portable electronic devices using various nanomaterials including carbon nanoparticles. Sensors are among the highly sought devices for different purposes in multi-disciplinary fields such as food industries and medical field [1]. Moreover, various reports on different environmental pollutants such as toxic volatile organic chemicals (VOCs) are often seen as one of the world largest problem. The amount of VOCs in the environment could be monitored using sensors. Usually, sensors make use of materials that can actively and/or selectively detect certain VOCs such as acetone, ethanol and toluene [2-4]. The materials used can be in different forms such as a composite or hybrid material [5].

The use of carbon nanomaterials-based composites in gas sensors is reported to tune the sensitivity towards various VOCs due to their various physicochemical properties [6, 7]. It is reported that when nanocarbons such as carbon nano-onions (CLCNOs) [8], carbon nanotubes [9], and carbon nanofibres [10] are used as composite material with polymers and metal oxides such as polyvinylpyrrolidone and zinc oxide [11]. The carbon backbone structure provide higher charge carrier mobility (e.g. ballistic electron transport) as well as low noise and thus promote the better sensing mechanism [12]. Hence, carbon nanomaterial-metal oxide based composites can be potentially used to develop room temperature gas sensors [13]. In most cases, gas sensors are fabricated using metal oxides nanoparticles for good performances towards detection of various VOCs [14]. Metal oxides are used for their physicochemical properties such as large surface to volume ratio, smaller particle sizes and chemical stability [15, 16]. However, while most metal oxides provide good sensing performances, they require elevated temperatures ($>100\text{ }^{\circ}\text{C}$) which lead to higher power consumption [17-19]. Moreover, other metal oxides such as manganese oxide

(MONRs) has poor gas performances when used as a thick active film which makes it difficult to study their gas sensing properties [20].

Hence, with its natural abundance, MONRs can be favorably used to form gas sensing nanocomposite. Considering the cost of the present gas sensors, there is a need to use inexpensive nanomaterials to fabricate user friendly sensing devices.

CLCNOs are among the class of spherical nanocarbons which can be used to form the active VOC(s) detecting material [21, 22]. CLCNOs possess fascinating and unique chemical and physical properties such as high electrical conductivity and large surface area [23]. Their synthesis involves the use of various methods including the various pyrolysis processes in which different shapes and sizes can be obtained (e.g. dense or solid CLCNOs) [24, 25]. Their synthesis through the pyrolysis method is considered as one of the facile and inexpensive methods since it makes use of simple apparatus [26]. Different carbon sources such as anthracene, naphthalene and pyrene have been reported for the synthesis of stable “soot” nanoparticles using the pyrolysis method [27, 28]. Moreover, pyridine has also been pyrolyzed for various purposes including the synthesis of nanoparticles [29, 30]. Pyrolysis of pyridine was selected and used in order to synthesize nitrogen doped CLCNOs (N-CLCNOs) in-situ (see **Figure 7.1**, for the general structure of pyridine). Thus, N-CLCNOs exhibit unique chemical and electrical properties that are important for application in gas sensors. This is possible since it can produce free radicals that can implement the cycloreversion to also change its molecular structure to the radical chain form [31]. Nitrogen containing CLCNOs were reported to have enhanced dispersibility and electrochemical properties [32, 33].

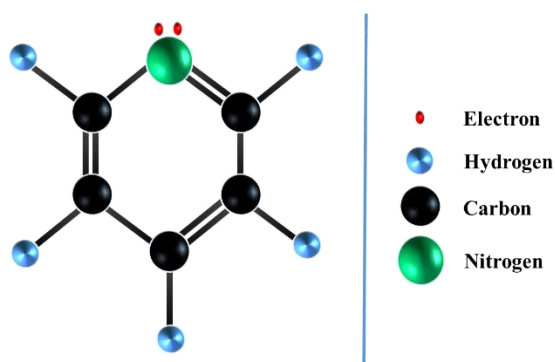


Figure 7.1: The general molecular chemical structure of pyridine [32].

Herein, the use of nitrogen doped CLCNOs (N-CLCNOs), MONRs and polyvinylpyrrolidone (PVP) composites as an active sensing material for the detection of VOCs at room temperature has been

explored [34]. MONRs composites with carbonaceous material such as carbon nano-onions (CLCNOs) can be investigated since MONRs can synergistically improve the electrical conductivity of CLCNOs due to its high porosity, larger surface area, structural flexibility as well as chemical stability [35, 36]. Notably, the crystallographic nature of MONRs exhibit different polymorphic forms such as α - and β -MONRs [37, 38]. Different MONRs polymorphs offer excellent physicochemical characteristics that makes the most stable MONRs forms at room temperature [39, 40].

The incorporation of the polymer in the composite will allow for metal oxide stabilization such that it can actively detect VOCs at room temperature [41, 42]. As such, it can be postulated that the N-CLCNOs/MONRs/PVP composite will offer better adsorption and desorption of oxygen molecules around sensing composite with the metal oxide. Moreover, the nitrogen carrying CLCNOs will further promote charge carriers mobility within the metal oxide based nanocomposite [43]. Interestingly, this is a first time report on the use of N-CLCNOs/MONRs/PVP composite for fundamental detection of acetone, ethanol, and toluene. Hence, the general hypothesis is that the synergistic activity of the N-CLCNOs and MONRs mixed with PVP will allow for fundamental detection of different VOCs (herein; acetone, ethanol, and toluene) at room temperature.

7.2. Experimental

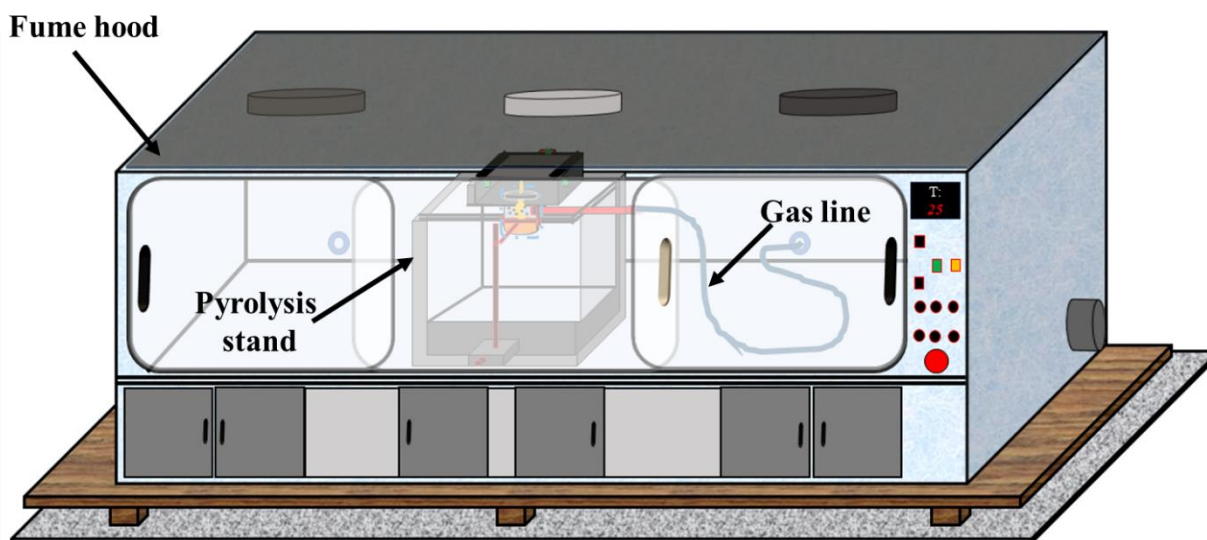
7.2.1. Starting materials

Anhydrous pyridine (C_5H_5N , 99.8%) supplied by the Merck (South African Company) and a fibre-glass wick (purchased from a local retailer) were used as received. A polished brass collecting plate and a steel-tube stand see designed with a circular shaped air-flame controlling ring were built in the University of the Witwatersrand physical sciences workshop as shown in **Scheme 5.1**. The compressed air was purchased from Afrox (South African company). Acetone, air, ethanol, hexane, manganese sulphate ($MnSO_4 \cdot H_2O$), polyvinylpyrrolidone (PVP), potassium permanganate ($KMnO_4$) and toluene were also purchased from Merck and were used as received.

7.2.2. Synthesis of N-CLCNOs using pyridine

About 5 mL of pyridine was transferred into a 10 mL glass container in which a fibre-glass wick was immersed and allowed to stand in the oil for 30 minutes such that it extracts the liquid by capillary actions and/or surface tension [44, 45]. The glass container was placed beneath the

acetone washed BCP at an optimized distance of ~40 mm between the glass nozzle and the BCP using the distance adjusting rod. Finally, the distance between the luminous zone of the flame and the collection plate was maintained at ~20 mm. The wick was ignited to produce a flame in a controlled fume hood (see **Scheme 7.1**).



Scheme 7.1: The fume hood flame pyrolysis set-up used during the pyridine flame pyrolysis process with detailed controlled-spray pyrolysis circuline container for controlling the flame shape.

In a typical experimental process, a circuline ring shown in **Scheme 5.1** was used to control the flame shape by flushing synthetic-compressed air around the ring's circular path that has air-spraying holes. The as-synthesized black carbonaceous material from pyridine was then collected continuously onto to BCP plate for 5 minutes. This was followed by collection of the product by scraping the product from the BCP using a solid-plastic spatula. The collected pyridine derived nanomaterial was labelled as the N-CLCNOs respectively.

7.2.3. Synthesis of metal oxide nanorods

Manganese oxide nanorods (MONRs) were synthesized using a method previously reported by Wang *et al.*, without any modification [46]. A hydrothermal synthesis process was followed by using a Teflon-lined hydrothermal autoclave. The autoclave was heated up to 160 °C and the reaction continued for 12 h (see discussion in **Section 5.2.3**).

7.2.4. Fabrication and testing of the sensing devices

The initial step involved the preparation of a mixed materials solution (i.e. composite solution), using N-CLCNOs, manganese dioxide (MONRs), polyvinylpyrrolidone (PVP) and dimethylformamide (DMF). DMF was used as the preferred solvent due to its ability to disperse MONRs together with N-CLCNOs. PVP was then used to stabilize the under room temperature conditions. For the preparation of N-CLCNOs based composite, a 1:1:3 ratio of N-CLCNOs:MONRs:PVP was added to 3 mL of DMF. The mixture was stirred for 12 h at room temperature followed by sonication for 1 h to obtain a homogeneous suspension of the composite. As discussed in **Section 5.2.4**, the electrodes were prepared and used to fabricate the N-CLCNOs/MONRs/PVP based gas sensor. The response of the sensing device was studied using the LCR meter by following all steps that are discussed in **Chapter 5**. Additionally, the required calculations (e.g. calculation of analytes' concentration) were done using formulae in **Section 2.1.2** accordingly [47-52]. Lastly, the time interval for the gas sensor's response (i.e. R_{meas}) to change from 10 to 90% of its final saturation value (i.e. R_f) after applying the stimulation as a step-function is given as the sensor's response time. In the case of a reversible system, it is then possible to also identify the time for the response signal to change from 90 to 10% that exists following the final saturation value regarded as the recovery time of the gas sensing system [53]. Thus in this study the gas sensor response and recovery time towards every analyte was determined following tests in which the sensor was exposed to increasing analyte concentration at 1 μ L intervals for seven injection steps. Every 1 μ L of the analyte was injected after 300s of exposing the sensor to the analyte environment in the sweep covered testing chamber. 300s was used to accommodate the sensor's response time before its saturation whereas about 150s was used to monitor for the sensor's recovery time.

7.3. Techniques used to characterize the nanomaterials used to form the sensing material

The structural morphology and characteristics of the CLCNOs produced were studied by using the scanning electron microscopy (SEM) technique and the instrument was operated at 30 kV in each case. The microscopy micrographs of CLCNOs and its metal oxide based composite were

ascertained by transmission electron microscopy (TEM) using a Tecnai G2 30ST operating at 200 kV. The quality and structural properties of CLCNOs (supported on a silicon wafer (2 mg sample holder)) and its metal oxide composite were investigated using a Jobin-Yvon T64000 Ultraviolet (UV) LabRam HR-micro Raman spectrometer with an Olympus BX41 microscope, that makes use of a liquid nitrogen cooled charge coupled device detector working at an excitation wavelength of 514.5 nm at room temperature. A Bruker D2 Phaser XRD that uses Cu-K α irradiation and operated at 30 kV with the X-ray tube at the current of 30 mA over a $10^\circ \leq 2\theta \leq 90^\circ$ scanning range was used to analyse the crystallographic nature of the CLCNOs based samples. A Micromeritics Tristar 3000 surface area and porosity analyser was used to determine the surface area and pore volume of CLCNOs (200 mg). Furthermore, the elemental composition of CLCNOs and its metal oxide composite surface analysis was achieved using two different techniques; (1) the FEI Nova Nanolab 600 FIB-SEM instrument as well as the FEI Quanta 450 FEG-SEM coupled with the energy dispersive spectroscopy (EDS) detector was used to determine the structural morphology of CLCNOs and their surface elemental composition respectively, (2) the Physical Electronics Quantum 2000 X-ray photoelectron spectroscopy (XPS), that uses a monochromatic Al K α source operated at 1486.7 eV.

7.4. Results and discussion

7.4.1. Structural morphology analysis of CLCNOs and MONRs

The microscopy micrographs shown in **Figure 7.2** reveal that the as-synthesized material exhibit nanoparticles that are clustered together to form larger conglomerates. The diameter of the nanoparticles were found to be less than 100 nm. However, there is no sign of particle size uniformity which is attributed to the formation of different quasi-spherical shapes and sizes of conglomerates. Hence, the TEM suggests that this material contains primary particles (PPs) with various sizes that create multiple particles cores as shown by arrows in **Figure 7.2(b)**.

This observation is indistinguishable from that was previously reported by Leidenberger *et al.*, based on the carbonaceous nanoparticles derived from diesel [54]. The larger nanoparticle conglomerates were formed with inter-linked or chain-like shapes. Moreover, it was also observed that the PPs forming conglomerates exhibit overlapping quasi-spherically shapes which can be ascribed to their nuclei coalescence that occurs during the combustion or pyrolysis process [55,

56]. The overlapping of PPs' nuclei is regarded as the primary source of the multiple particles cores that result in the formation of larger conglomerates.

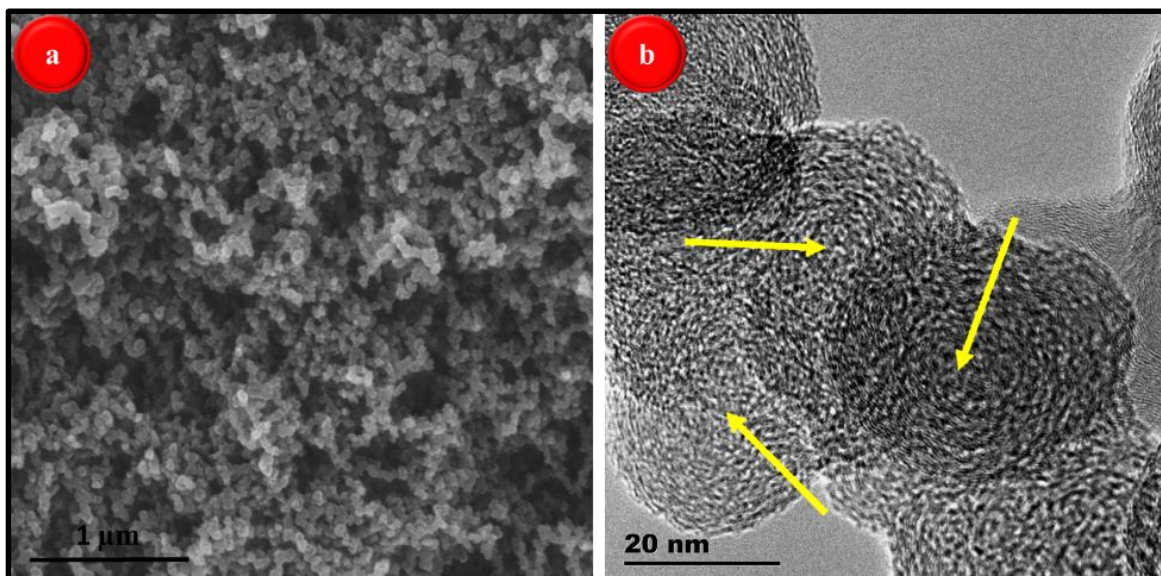


Figure 7.2: (a) SEM micrograph of the as-synthesized N-CLCNOs, and (b) TEM micrograph of conglomerated and multi-layered N-CLCNOs.

In this study, it was observed that the pyridine derived carbon nanoparticles are dense or solid connected like chains and partly form larger multi-layered carbon conglomerates as shown by the two dimensional (2D) micrograph in **Figure 7.3(a)**. The investigation of the particle sizes distribution reveals that, the obtained N-CLCNOs nanoparticles are less than 80 nm (i.e. 69.6 ± 3.5 nm) as shown by the circled particles regions in **Figure 7.3(a)** along with the particle size distribution plot in **Figure 7.3(a)** insert. This results show that the smaller nanoparticles in the group of spherical carbon nanoparticles have been formed with comparable particles sizes to other spherical carbon nanoparticles (e.g. solid carbon nanospheres) [57-59].

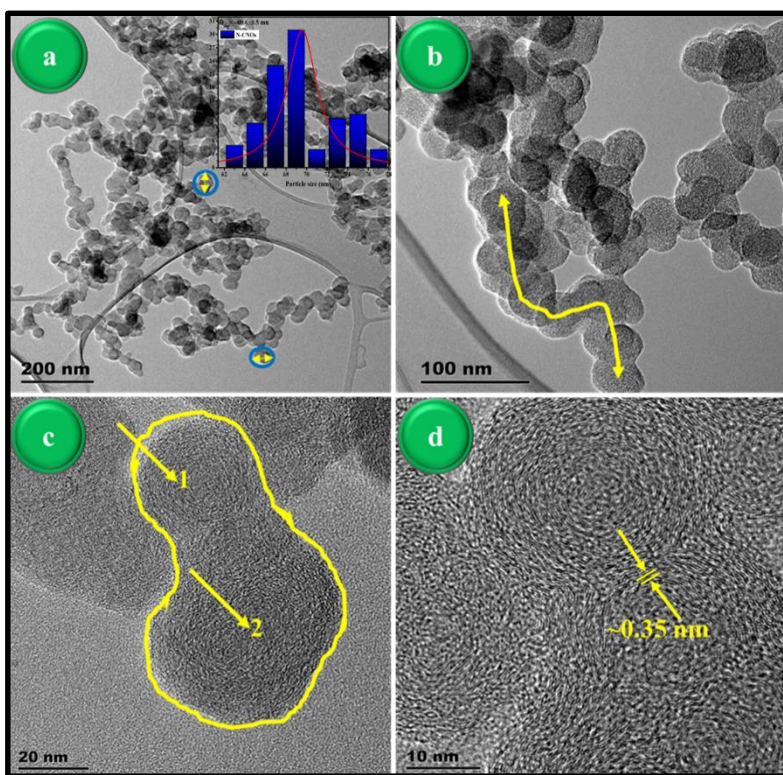


Figure 7.3: TEM micrograph of; (a) as-synthesized N-CLCNOs at low magnification with the particle size distribution curve insert, (b) chain-like co-joined closed cage quasi-spherical CNO structures, (c) multi-layered regions and dual centres per particle, and (b) particle inter-layer spacing of short range multi-layered N-CLCNOs.

Furthermore, it is evident that the N-CLCNOs particles are overlapping with one another to form different shapes of carbonaceous conglomerates as shown in **Figure 7.3(a)**. Hence, a single or lone nanoparticle is hardly seen in the microscopy results which suggest that there is no mono-dispersity of the CLCNOs particles. This suggestion is supported by the results that indicates that the as-prepared N-CLCNOs material exhibit chain-like co-joined closed cage quasi-spherical structures embedded on amorphous carbon mass (see chain-like connection arrow in **Figure 7.3(b)**).

Upon detailed structural analysis, it was also observed that every N-CNO particle exhibit two distinct multi-layered regions as shown in **Figure 7.3(c)**. The micrograph presents the dual existence of inner core and an outer shell in which the inner core contains a number of fine short-range multi-layers for every nanoparticle (see arrow 1 and 2 in **Figure 7.3(c)**). The presented multi-layered regions are suggested to be covering the nucleus of each nanoparticle with the inter-layer spacing of ca. ~ 0.35 nm as shown in **Figure 7.3(d)**. It can be seen that the outer region of every particle is mainly composed of disordered multi-layers that are found towards the external outer surface of every CNO. Moreover,

some amorphous and graphitic crystallites exist in the outer shells regions which promotes the turbostratic nature of these nanoparticles. Hence, these turbostratic nanoparticles bear fragmented carbon properties which is one of the important physical property of this material. The porosity property can be attributed to the CLCNOs particles surface roughness which also provides the defective sites of these nanoparticles. The presented structural morphology suggests that the nanoparticles physical properties allows for their various application including in VOCs adsorption related studies [60]. TEM micrographs of the CLCNOs/MONRS/PVP are shown in **Figure 7.4**. It is evident that the as-synthesized MONRs have different sizes and/or length as shown in **Figure 7.4(a)** [61, 62]. It is suggested that the MONRs particle shape and sizes allows for various packing arrangement in the N-CLCNOs composite (see **Figure 7.4(b)**).

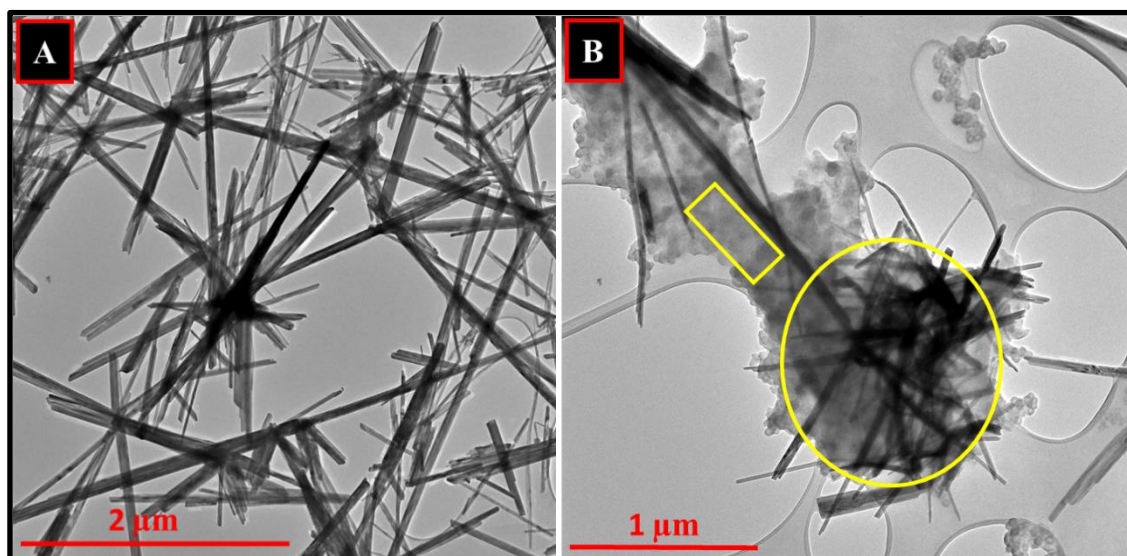


Figure 7.4: Low magnification TEM micrograph of; (a) as-synthesized MONRs, and (b) MONRs/N-CLCNOs/PVP composite.

In addition, **Figure 7.4(b)** shows that the structural shapes of CLCNOs and MONRs remain maintained in N-CLCNOs/MONRs/PVP composite as shown by the indicated rectangular and circular region respectively. It is further evident from SEM result that MONRs are supported onto N-CLCNOs forming a blend of nanorods and quasi-spherical nanoparticles as shown in **Figure 7.5**.

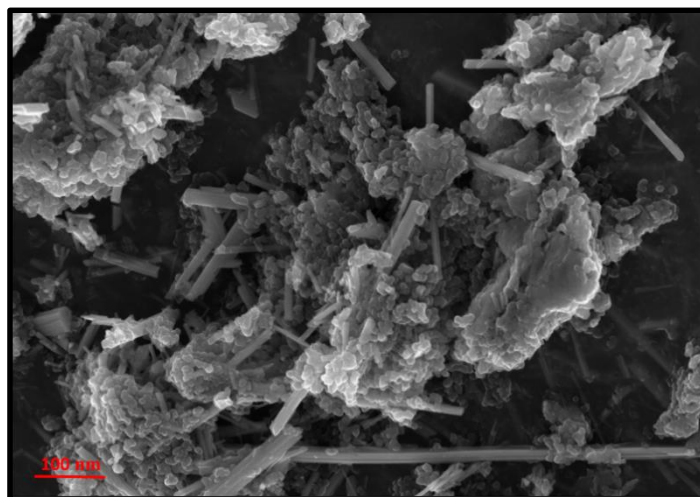


Figure 7.5: SEM micrograph of N-CLCNOs/MONRs/PVP composite.

Therefore, N-CLCNOs particles allows for chemical interaction of MONRs surfaces by providing the inter-linked embedding carbonaceous surfaces. Further investigations on the elemental composition of the N-CLCNOs-MONRs composite was carried out using the EDS technique. The EDX spectra shown in **Figure 7.6** reveal that both materials analysed contained carbon nanoparticles. The EDX spectrum in **Figure 7.6(a)**, indicated that when the area that only contains carbon nanoparticles was analysed, the kind of nanoparticles present in the sample carry nitrogen and oxygen atoms on their structural surfaces. This observation can be ascribed to the presence of different functional groups (e.g. carbonyl and nitroxy groups) provided by pyridine that was used as the pyrolysis carbon source. On the other hand, the EDX spectrum shown in **Figure 7.6(b)** indicates that the composite is formed by carbon, oxygen and manganese with no traces of nitrogen which might be chemically hindered by the presence of the polymer (i.e. PVP). Moreover, it is evident from the EDX spectrum in **Figure 7.6(b)** that there are two types of manganese detected namely α -Mn and the β -Mn. Thus, it can be deduced that the composite contains the α -MONRs and the β -MONRs.

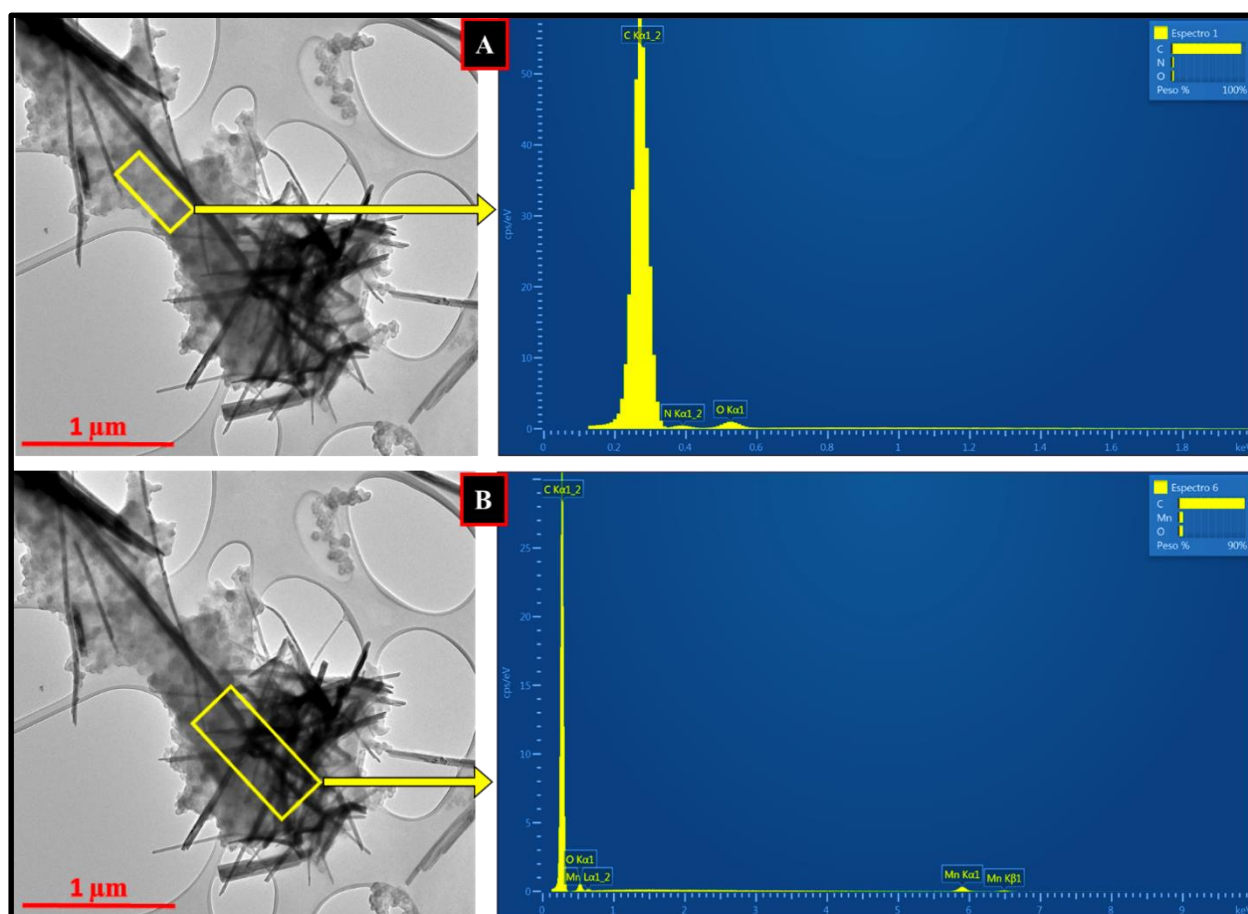


Figure 7.6: The EDX spectrum and low magnification TEM micrograph of; (a) as-synthesized N-CLCNOs with MONRs, and (b) MONRs/N-CLCNOs/PVP composite.

Raman spectra were obtained and used to further analyse the degree of atomic order in the structural matrix of the nanoparticles formed. The results in **Figure 7.7(a)** show two Raman prominent peaks commonly known as the D- and G-band identified for carbonaceous nanomaterials (i.e. herein N-CLCNOs) [63, 64]. The peaks observed around 1338 cm^{-1} represent the density of induced disorders or defects from C–C or C–N vibrations modes corresponding to the disruptions in sp^2 whenever the newly hybridized carbon bonds such as dangling bonds, sp^3 bonding are formed [63]. This band can also signify the presence of structural vacancies, and carbon rings other than hexagon [63]. On the other hand, the observed peaks around 1580 cm^{-1} are labelled as the G-bands ascribed to the C=C graphite carbon in-plane vibration modes of the carbon material with sp^2 orbital structure [64]. Notably, the D- and G-band full width at half maximum (FWHM) were higher than ca. 260 and 80 respectively for both samples as shown in **Table 7.1**. Thus, the G-band FWHM for both samples were lower than those of the D-bands. This signifies

that both samples presented sharper G-bands even though they showed different intensities (see **Figure 7.7(a)**).

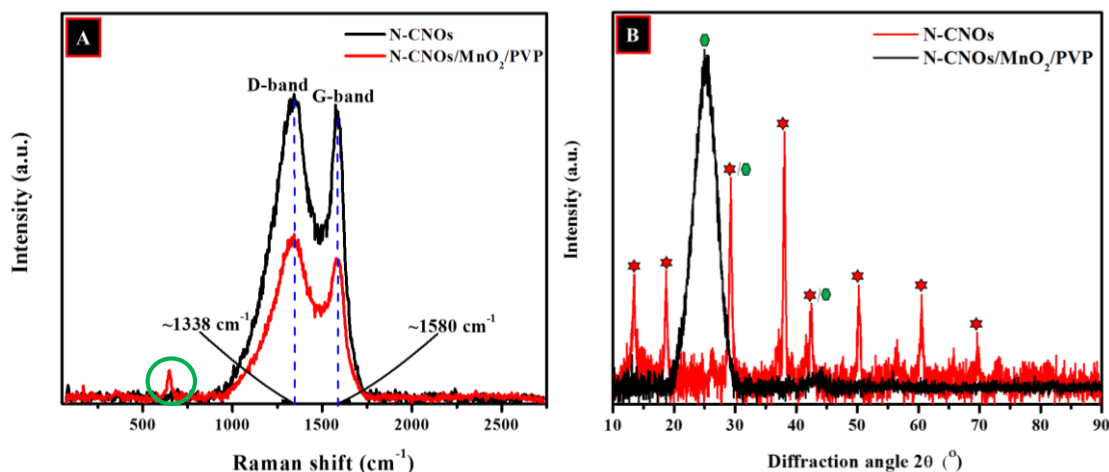


Figure 7.7: (a) the Raman spectra of as-synthesized N-CLCNOs, and (b) MONRs/N-CLCNOs/PVP composite, and (b) PXRD patterns of as-synthesized N-CLCNOs, and (b) β -MONRs/poliCLCNOs/PVP composite.

This suggests that the structural matrix of N-CLCNOs and its MONRs composite exhibit sp^2 hybridized carbon atoms. Additionally, the data in **Table 7.1** indicates that the D-band FWHMs are trice higher than those of the G-band and this can be attributed to the increased amount of sp^3 C-C and/or C-N vibration modes which can contribute to the detected structural defects or disorders. Moreover, this observation can be attributed to the exposure of the in-plane terminations of either pentagonal or hexagonal carbon network of N-CLCNOs outer shells as well as possible amorphous carbon nanoparticles [64, 65].

The area ratios of the D-band and the G-band (I_D/I_G) were significantly used to quantify the degree of graphitization of as-synthesized N-CLCNOs and its MONRs-PVP composite [63-65]. It can be seen that the I_D/I_G values for both samples are greater than 1 as shown in **Table 7.1**. The calculated $I_D/I_G > 3.5$ for both samples implies a low degree of graphitization which can be attributed or associated to long-range structural disorder of the carbon nanoparticles shown by TEM micrographs. Thus, the obtained I_D/I_G gives the direct relationship of the extent to which the defects or disorders are present in the form of sp^3 hybridized C atoms as well as shorter graphitic fragments [45, 66]. In the case of the N-CLCNOs/MONRs/PVP composite, a higher defects density was higher (ca. $I_D/I_G = 4.05$) as compared to bare N-CLCNOs. This further suggests that the physical

nanoparticles mixture of the composite contain more nanoparticulate structural defects which possibly allows for increased molecular adsorption and/or attachment sites.

As shown in **Figure 7.7(b)**, the PXRD patterns for N-CLCNOs and its MONRs composite in which the bare N-CLCNOs pattern presents the two prominent peaks for polycrystalline carbon material around 25 and 44°. These peaks can be assigned to the 002 and 004 planes of carbon nanoparticles. Thus, the appearance of peak centred at $2\theta \approx 44^\circ$ signifies that the CLCNOs produced contain moderate graphitic carbon domains. When looking at the PXRD pattern obtained for the composite, it presents multiple peaks which identifies the presence of β -MONRs as indicated by stars in **Figure 7.7(b)**.

Table 7.1: Raman data of N-CLCNOs and N-CLCNOs/MONRs/PVP composite.

Sample	Raman shift (cm ⁻¹) D-band	Raman shift (cm ⁻¹) G-band	I_D/I_G	FWHM	FWHM
				D-band	G-band
N-CLCNOs	1337.6	1586.8	3.78	267.5	81.2
N-CLCNOs/MONRs/PVP	1337.8	1586.41	4.05	263.0	86.1

I_D: area of the D-band, *I_G*: area of the G-band, *I_D/I_G*: ratio of the areas (i.e. for D-band and G-band respectively).

The C, N and O chemical environment on the N-CLCNOs surfaces was determined using the XPS technique which further supports the elemental composition data from EDX analysis as shown in **Figure 7.8**. The XPS data obtained revealed that the surface characteristics of as-synthesized N-CLCNOs exhibit various elemental composition which are mainly the carbon and oxygen atom arrangements along with minor presence of nitrogen atoms (see **Figure 7.8**) [67]. Thus, the detection of N atoms also confirms and signifies successful in-situ nitrogen doping of CLCNOs.

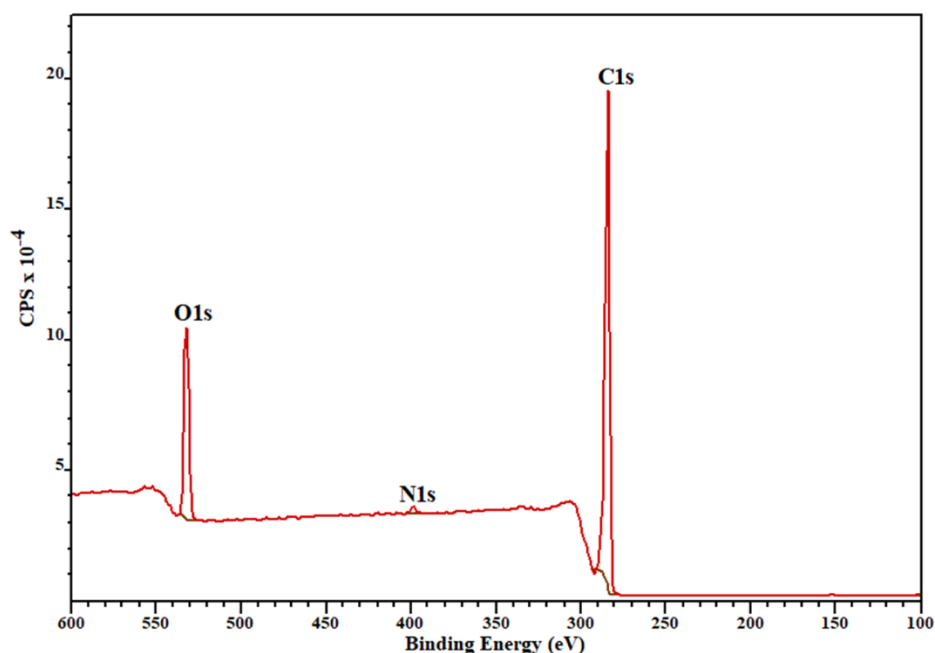


Figure 7.8: The XPS survey scan of N-CLCNOs synthesized using the pyridine pyrolysis method.

The C1s peak was deconvoluted into five bonding states peaks that represents different C atom bonding configurations present in the structural matrix of N-CLCNOs as shown in **Figure 7.9(a)**. The signals obtained reveal that N-CLCNOs exhibit sp^3 hybridized C atoms as suggested by the presence of D-band given by the Raman data [68, 69]. The results in **Figure 7.9(a)** presents the presence of C-C, sp^2 -C, N- sp^3 -C or sp^3 -C, C-O and O-C=O which were indicated by the peaks positioned at 283.59 eV, 284.41 eV, 285.06 eV, 285.78 eV, and 288.01 eV respectively. Given this information, it is suggested that the lower binding energy region (i.e. <284.45 eV) mostly correspond to the sp^2 C-C bonds and the higher binding energy region (i.e. >285.00 eV) correspond to sp^3 C-C bonds [70, 71]. Moreover, the peak centered at 285.06 eV can be assigned to carbon bonded to the most electronegative nitrogen atoms that form sp^3 C-N bonding configurations.

The deconvoluted N1s peak reveals that N-CLCNOs contains different C-N bonding states. This can be seen in **Figure 7.9(b)** in which four prominent peaks are presented and assigned to different C-N bonding states. In this case, detected C-N bonding states were assigned to; (i) pyridinic-N at 397.81 eV in which the N atom can contribute an electron to the p-system, (ii) pyrrolic-N at 398.71 eV in which the N atom can contribute two electrons to the p-system, (iii) graphitic-N at 400.24 eV with the N atom substituting the C atom in the CLCNOs structural matrix [45, 89] and (iv) pyridinic oxide bonds (NO_x) at 403.38 eV which can be ascribed to the oxygenation of pyridinic-N (see **Figure 7.9(b)** and **(d)**) [72-75]. Furthermore, the obtained data reveals that N-CLCNOs

comprised of 45.25% pyridinic-N, 37.80%, pyrrolic-N, 4.97%, graphitic-N and 14.98% pyridinic oxide bonds as shown in **Figure 7.10(b)**. The presence of a higher percentage of pyridinic-N which is also associated with the pyridinic-N⁺-O⁻ bonding configuration in the on the N-CLCNOs surfaces can be attributed to the dominance of oxygen atoms bonded to their surface edge defects (see **Figure 7.10(b)**). Notably, the data shows that the overall material is dominated by carbon with its highest percentage at 76.81% followed by 10.12% of oxygen along with 11.58% of oxygen-carbon as shown by the pie graph in **Figure 7.10(a)**. Thus, the O1s XPS spectrum shown in **Figure 7.9(c)** indicates that most of the oxygen atoms are bonded to the carbon atoms with the C-OH as well as O-C=O bonding configurations that are indicated by the peaks positioned at 531.89 eV and 533.29 eV respectively [76, 77]. The existence of different bonding configurations in N-CLCNOs allows for improved conductivity since they exhibit a higher pyridinic-N content that provides a larger edge plane exposure of the nanoparticles [78].

In addition, the total surface area and pore sizes of the as-synthesized N-CLCNOs and the composite material were investigated using the BET surface characterization technique [69, 79]. The surface area of N-CLCNOs (i.e. 294.64 m²/g) was about fifteen times higher than that of its metal oxide based composite (i.e. 19.60 m²/g). The BET particle pore sizes measurement further revealed that N-CLCNOs has pore sizes averaged to 3.18 nm, with the pore volume of 0.23 cm³/g whereas MONRs sample that has a total surface area of 33.34 m²/g exhibit averaged pore size of 0.23 nm, and the pore volume of 21.77 cm³/g. Interestingly, the pore size and volume of the metal oxide based composite were found to be 0.13 nm and 33.17 cm³/g respectively. This is an alternative indication of decreased pore sizes as well as the pore volume increment whenever the as-synthesized N-CLCNOs and MONRs are used in a nanocomposite. This observations result from the use of a stabilizing agent (i.e. PVP), which decreases the available pores by occupying the all possible pores and it alternatively increases the surface volume of the whole composite.

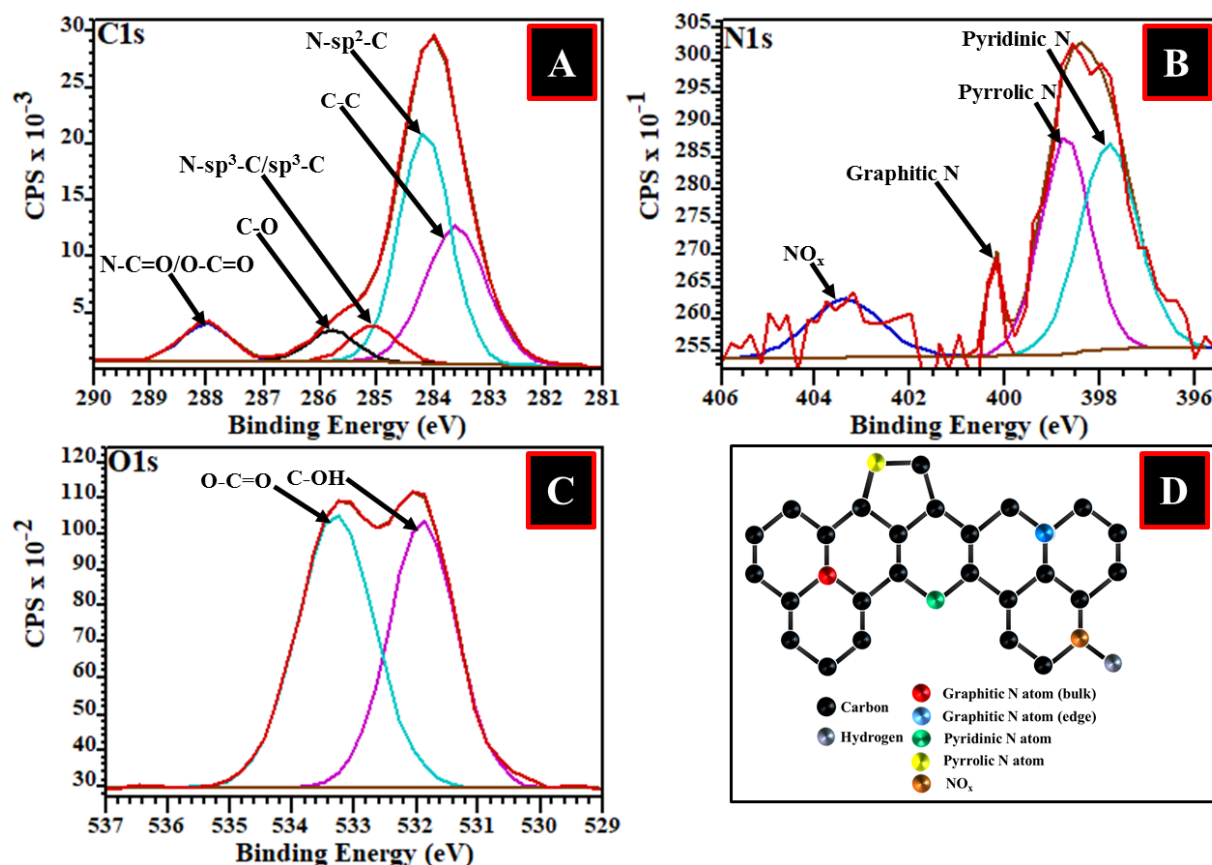


Figure 7.9: XPS survey scan of N-CLCNOs' deconvoluted spectrum for; (a) C1s, (b) N1s, (c) O1s, and the (d) proposed N configurations exhibited by N-CLCNOs.

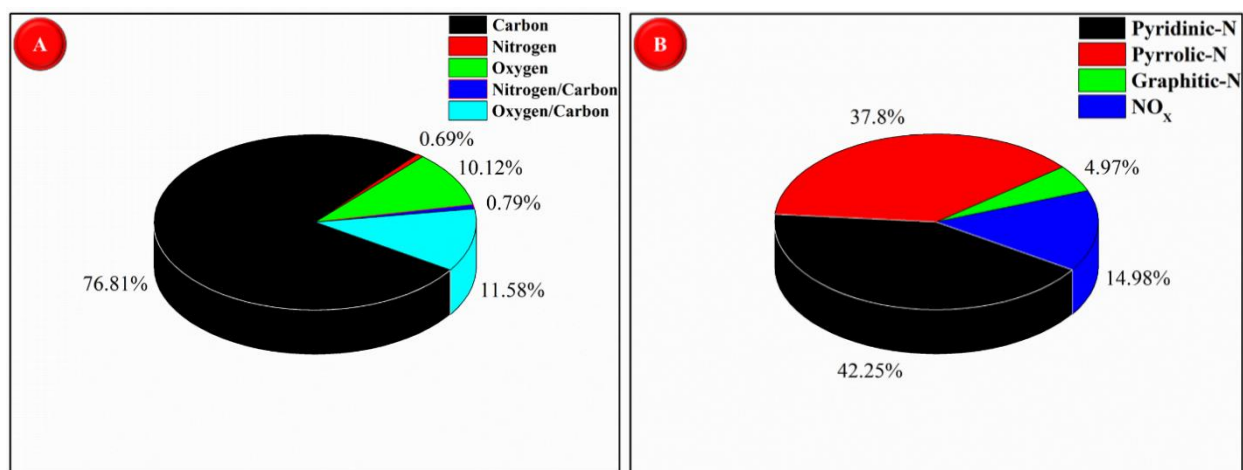


Figure 7.10: The pie chart that represents the XPS survey scan of; (a) the elemental composition percentages, and (b) different types of nitrogen percentages for the as-synthesized N-CLCNOs.

Therefore, it is suggested that the surface properties of N-CLCNOs/MONRs/PVP composite (i.e. the surface area, pore size and volume) are greatly influenced by the individual nanomaterials used for the mixture since the material such as N-CLCNOs may provide their curvature, shape and direct contact area which contribute directly to the surface properties of the composite formed in the presence of a polymer (herein; PVP).

7.4.2. Electrochemical tests for detecting VOCs: Chemiresistance measurements of the p_{oli} CLCNOs sensing device

In this study, the main focus was on investigating the chemiresistive behavior of the N-CLCNOs/MONRs/PVP composite. The performance characteristics of the gas sensor fabricated with this composite was investigated following the static and dynamic characteristics [80, 81]. It was important to investigate the best operating frequency of the sensing device using the highest signal to noise ratio (SNR) since the change in resistance of this devices does not only depend on the analyte's concentration. This follows the static characterization in which the different quantities (e.g. linearity and sensitivity) were measured at constant time intervals and those quantities slowly changes with time. The SNR plot indicates that the prepared sensing device using the given IDE has the highest SNR at 3 kHz as shown in **Figure 7.11(a)**.

Following the SNR studies, 3 kHz was selected as the optimal working frequency for the detection of the three analytes. The use of this frequency was preferred because it allowed for facile fabrication of a sensing device that allows for use of less electrical power [82]. In most cases, the sensing devices that are fabricated using n-type metal oxide semiconductors have negative charge carriers as the majority charge carriers and in their presence, an increase in conductivity occurs in the presence of a reducing gas [83]. Since the composite of interest contains MONRs, it is evident the resistance of the sensor decreases as the concentration of different analytes increases whenever 3 kHz is used during chemiresistance measurements (see **Figure 7.11(b-d)**).

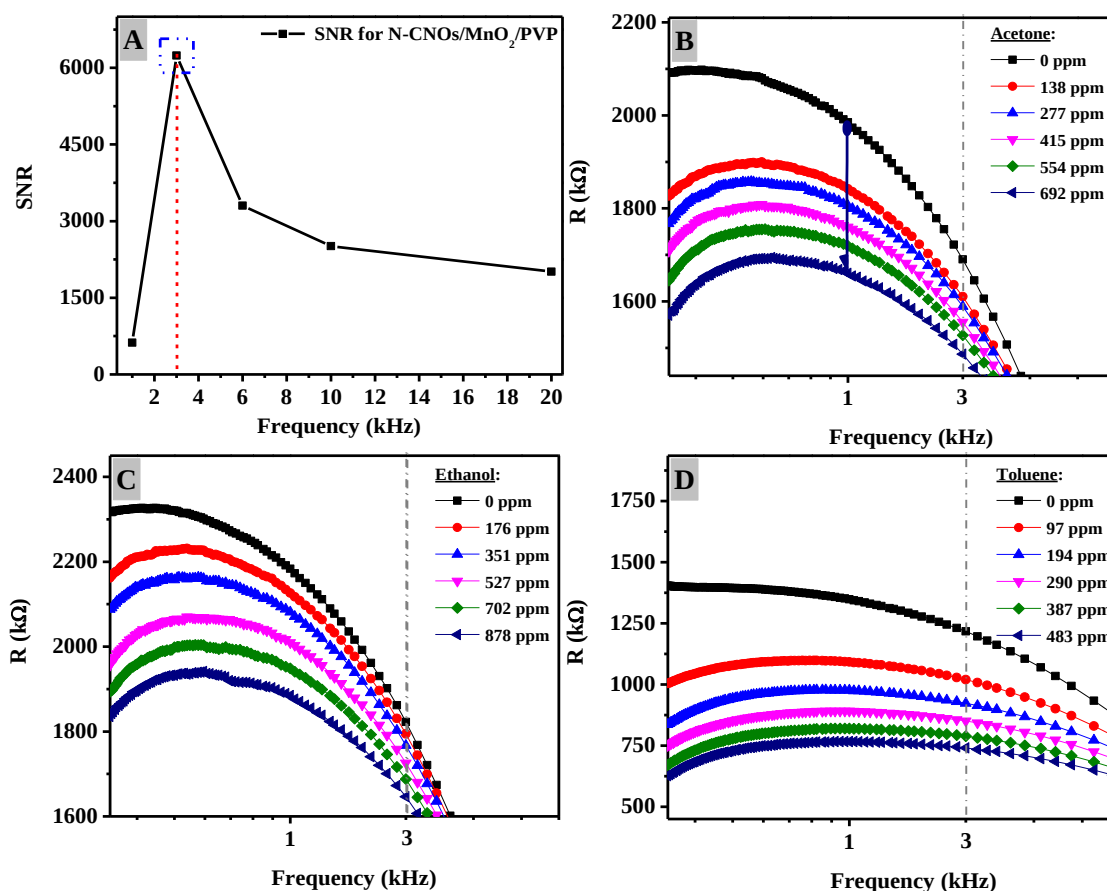


Figure 7.11: (a) SNR plot representing sensor's highest response at 3 kHz and the zoomed plot of resistance (R in $k\Omega$) as a function of frequency for detecting; (b) acetone, (c) ethanol, and (d) toluene, at varied analyte concentrations.

This trend suggests that the detected analytes exhibit properties (e.g. functional groups) that facilitates molecular interaction with the n-type MONRs which were used to make the active sensing material. Hence, this reveals that the results shown in **Figure 7.11(b-d)** reveal similar response towards different analytes. Interestingly, it was identified in addition that the response towards acetone, ethanol and toluene revealed alternating changes in resistance as shown in **Figure 7.12(a), (c) and (d)**. In addition, it was seen that the response towards different analytes showed a decrease in resistance between 0.4 and 6 kHz whereas an increase resistance was observed between 6.5 and 20 kHz as the selected measured frequency range for every analyte at varied concentrations as described by the zoomed acetone response plot in **Figure 7.12(b)**. Thus, this evidence suggests a p-type semiconducting-like sensing behavior whenever a working frequency higher than 6.5 kHz is used. Moreover, the differences in the shape of the baseline (i.e. resistance (R) versus frequency

(f) curves at 0 ppm) are as the result of potential kinetically controlled states including each analytes chemisorption and/or physisorption effects.

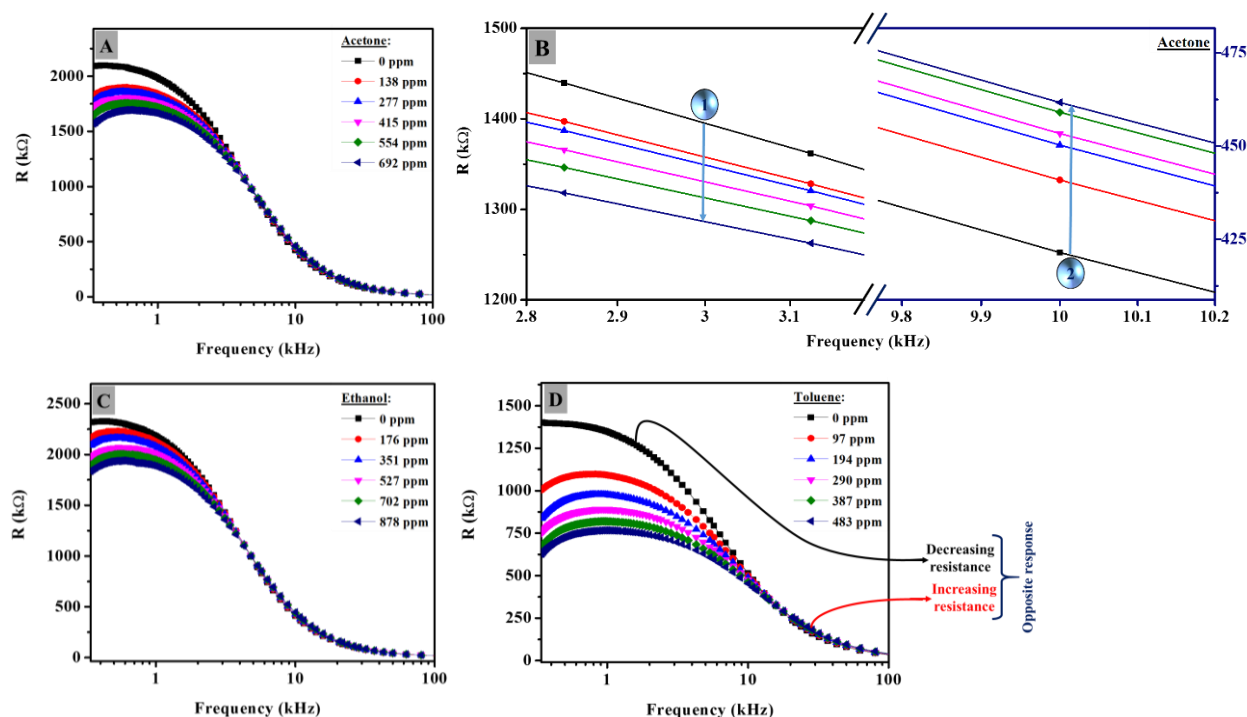


Figure 7.12: Plots of resistance (R in $k\Omega$) as a function of frequency for detecting; (a) acetone, (b) acetone (zoomed frequency regions), (c) ethanol, and (d) toluene, at varied analyte concentrations.

Furthermore, the results in **Figure 7.13** also shows similar shape of the baselines for the blank measurements. In this case, the response ($\Delta R/R_0$) as a function of frequency were also measured using different analytes. The results obtained suggest that the adsorption of different analyte molecules on a carbon-based sensing material selectively depends on several parameters such as the dipole-moment and the porosity of the carbonaceous surface that is present in the sensing composite [84]. The results in **Figure 7.13(a-c)** also show that whenever the sensor is operated between 0.3 and 6.5 kHz, the resistance decreases as the concentration of the analyte increases for all analytes tested. This observation further suggests an n-type behavior of the active sensing composite used for the sensor operated at lower frequencies (i.e. <6.5 kHz). However, when the device is operated between 6.5 and 20 kHz, the resistance increases as the concentration of the analyte increases for all analytes tested. This is an interesting behavior which suggest that this kind of a sensing composite can used to respond towards acetone, ethanol and toluene as either an n-

type or p-type active sensing material. Thus, the type of interaction between the analytes molecules and the adsorbed oxygen carrying ions on the surface of the sensing material play a significant role in terms of the sensing response. Depending on the frequency used, there exist electron donating or withdrawing effect induced by the analyte molecules which can favor n- or p-type response. However, it is always best to use the frequency that gives higher SNR for increased sensor's response. In summary, the results shown in **Figure 7.13(d)**, it can be also be seen that at 3 kHz the response ($\Delta R/R_0$) decreases as the concentration of the analytes used increases. These results also show that this kind of a sensing device is able to detect toluene faster than the other analytes (i.e. acetone and ethanol) as revealed by the stepper line plot. In this case, the dominating detection of toluene is followed by that of acetone with ethanol being the least detected. The observed trend can be attributed to various electron donating effects provided by each analyte. Toluene can easily react with active adsorbing sites that are available on the surface of the sensing composite.

Most of the active sites are on the surfaces of the N-CLCNOs-aggregates that are dominated by pyridinic nitrogen atoms which can also facilitate the electron exchanges during the chemical interaction between the analyte and the N-CLCNOs-aggregates based composite. Moreover, some of the active sites are on the surfaces of the active composite can be provided by the semiconducting MONRs. It is suggested that the ionized surface attached species are responsible for the breaking down of every analyte molecule in order to adsorb any electron donating or withdrawing groups. This results are supplemented by the observed static characteristic sensitivities towards every analyte derived from the sensor's response ($\Delta R/R_0$). As shown in **Figure 7.14**, the sensitivity towards toluene is higher than those of the other two analytes.

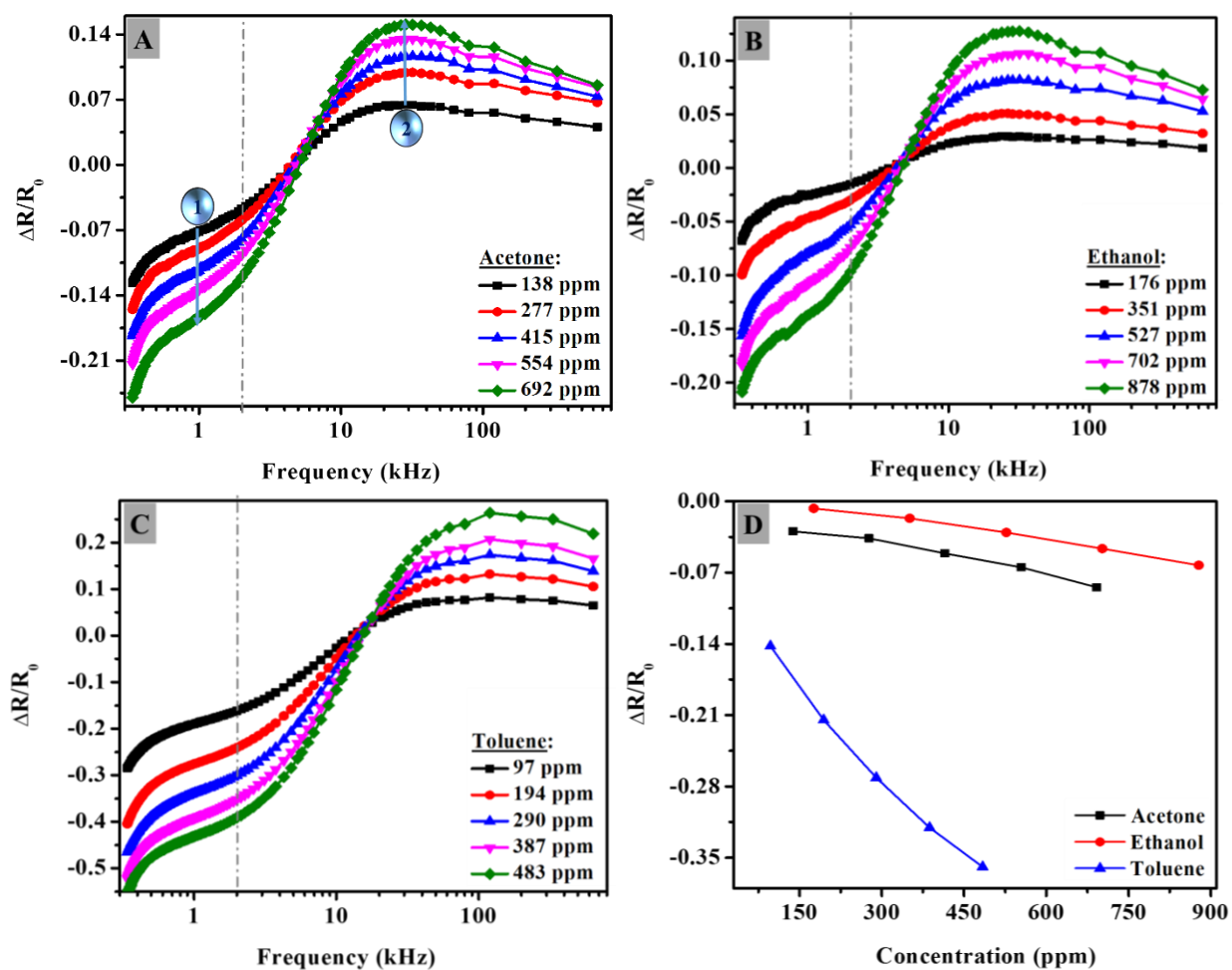


Figure 7.13: Plots that indicate the sensor's response ($\Delta R/R_0$) towards varied analyte concentrations as a function of frequency for detecting; (a) acetone, (b) ethanol, (c) toluene, and the (d) comparison plot showing the response ($\Delta R/R_0$) as a function of different analytes concentrations.

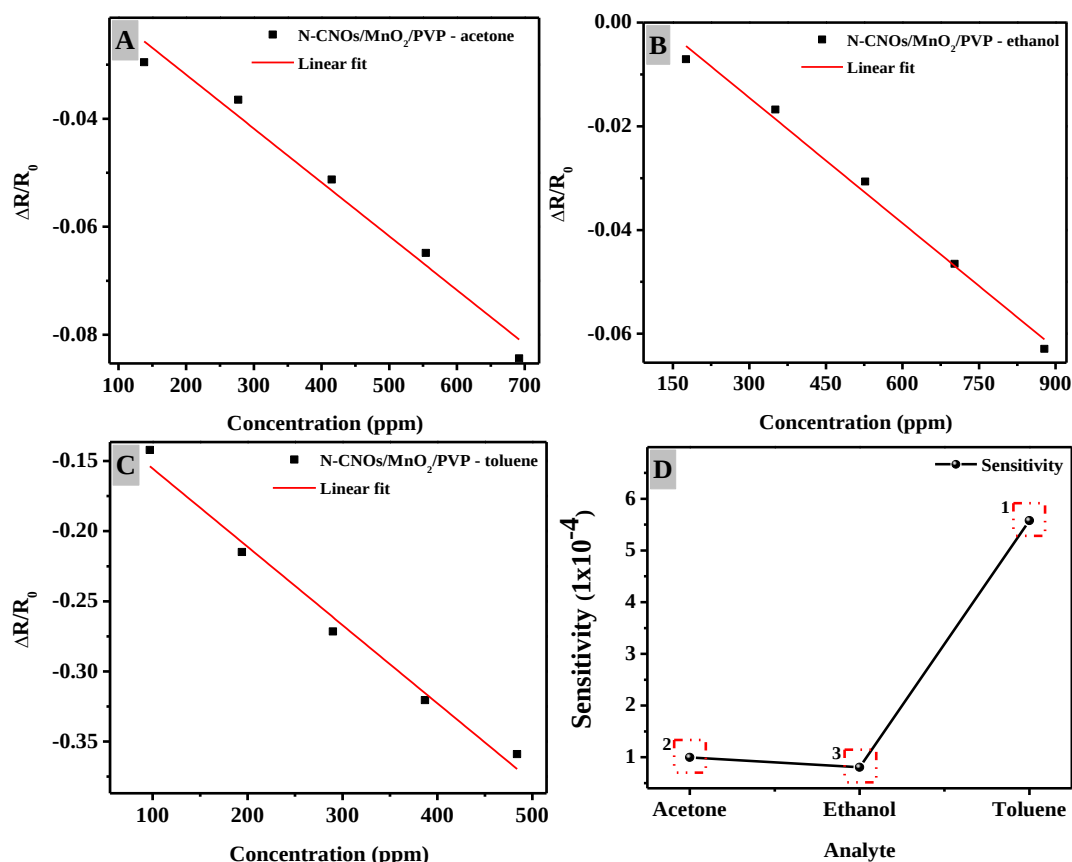


Figure 7.14: Plots shows sensor's response ($\Delta R/R_0$) towards; (a) acetone, (b) ethanol, and (c) toluene as a function of varied analyte concentrations with the respective response slopes and the (d) sensitivity comparison plot for different analytes used.

With the observation that the resistance and response results obtained revealed an n-type behavior for all sensors operated at 3 kHz as shown by a decrease in resistance with increasing analyte concentrations. This observation was then followed by determinations of the sensitivity of the sensor towards different analytes. The change in each sensor's response per concentration unit of the analyte was determined as the sensor's sensitivity (S) using the slope of a calibration curve. The results in **Figure 7.14** reveals that there is a significant difference in terms of the sensitivity towards acetone, ethanol and toluene. The sensor is highly sensitive towards detecting toluene ($S_{\text{toluene}}: 5.58 \times 10^{-4} \text{ ppm}^{-1}$) as compared to the detection of acetone and ethanol. The sensitivity of acetone and ethanol were found as $S_{\text{acetone}}: 9.96 \times 10^{-5} \text{ ppm}^{-1}$ and $S_{\text{ethanol}}: 8.06 \times 10^{-5} \text{ ppm}^{-1}$ respectively. Thus, this shows that the sensitivity towards acetone and ethanol were lower than those of toluene. Hence, the decreasing order of sensitivities towards different analytes was

obtained as $S_{\text{toluene}}: 5.58 \times 10^{-4} \text{ ppm}^{-1} > S_{\text{acetone}}: 9.96 \times 10^{-5} \text{ ppm}^{-1} > S_{\text{ethanol}}: 8.06 \times 10^{-5} \text{ ppm}^{-1}$ (also see **Figure 7.14(d)**).

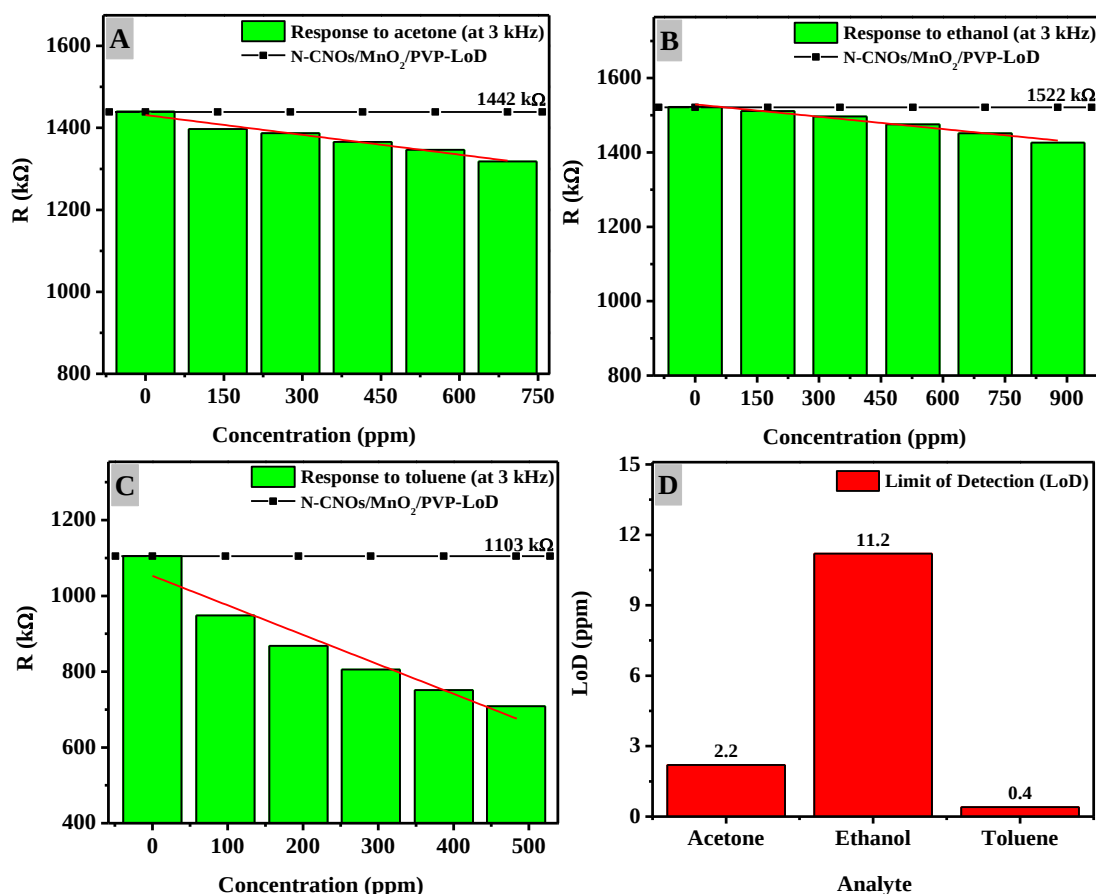


Figure 7.15: Graphs of resistance at 3 kHz as a function of different analyte concentrations for; (a) acetone, (b) ethanol, (c) toluene, in which the black horizontal line indicates the estimated LoD resistance for every measured analyte respectively, and (d) LoD comparison bar graph for the three analytes.

The lowest amount of every analyte in the detection system that is significantly different from the blank was determined using the LoD formula (see **Section 5.2.4**). As shown in the above **Figure 7.15**, the LoD results for all analytes testes indicates that the lowest LoD is toluene (LoD: 0.4 ppm). Interestingly, this means that the sensor is mostly sensitive for detecting toluene while being capable of identifying its molecules at lower concentrations (i.e. <1 ppm). Furthermore, the summary in **Figure 7.15(d)** also reveals that as the sensor has the second highest sensitivity towards acetone it also has the second lowest LoD (i.e. 2.2 ppm). This can be associated with the presence of easily available electron withdrawing groups from acetone and toluene. The easily

generated and available groups rapidly interact with the active sites on the N-CLCNOs/MONRs/PVP composite surface edges.

The performance characteristics of the sensor was further investigated using the dynamic characteristics [80, 81, 85]. Following the selection of 3 kHz as the best operating frequency for the sensing device using the highest signal to noise ratio (SNR) results, the dynamic characterization in which the different quantities (e.g. linearity and sensitivity) were measured. In this case, the time factors (i.e. response time and recovery time) were used study the speed of the sensor's response and recovery by resistance following each analyte detection. Thus, the speed at which the sensor will detect every analyte and will be ready to measure again is an important dynamic characteristic of the sensor's performance. Hence, this type of measurement indirectly shows the adsorption dynamics of the analyte molecules by the active material, from the non-interaction state up to the dynamic equilibrium. The calculations of time-related parameters are illustrated in **Figure 7.16(d)** in which the response time is defined as the time needed to achieve 90% of the saturation response after exposure to the analyte, whereas the recovery time is defined as the time required to recover 90% of the response after analyte exposure interruption as briefly explained in **Section 7.2.4**.

The results in **Figure 7.16(a-c)** also reveal that all analytes interact with the sensing material as shown by the change in resistance with increasing time. It is evident that the sensor responds quicker towards ethanol (at 204s) with the second most recovery time towards ethanol as shown in **Figure 7.17(b)**. This device has the faster recovery time towards acetone detection (at 68s, see **Figure 7.17(d)**). This observation depends on the molecular interaction between the analyte's molecules and the sensing composite. In each case, the analyte molecules sieve through the sensing composite and rapidly occupy its active sites by also following the Knudse diffusion effects [86]. It was noticed that the saturation or steady state of the sensor occurred for about 70s for all analytes. The observed signal intensity is related to interaction among different dipole moments of the analytes and the active layer which involves the physisorption or chemisorption properties of the active material. One other significant information when analyzing the response and recovery times in order to discern the type of interaction between the active layer and the analyte is; (1) whenever the interaction between the analyte and sensing material is weak, the signal returns to the initial

response value, but if (2) the interaction is strong, the signal does not return to the initial value and this leads to the need of further active layer treatments which is not favorable [87, 88].

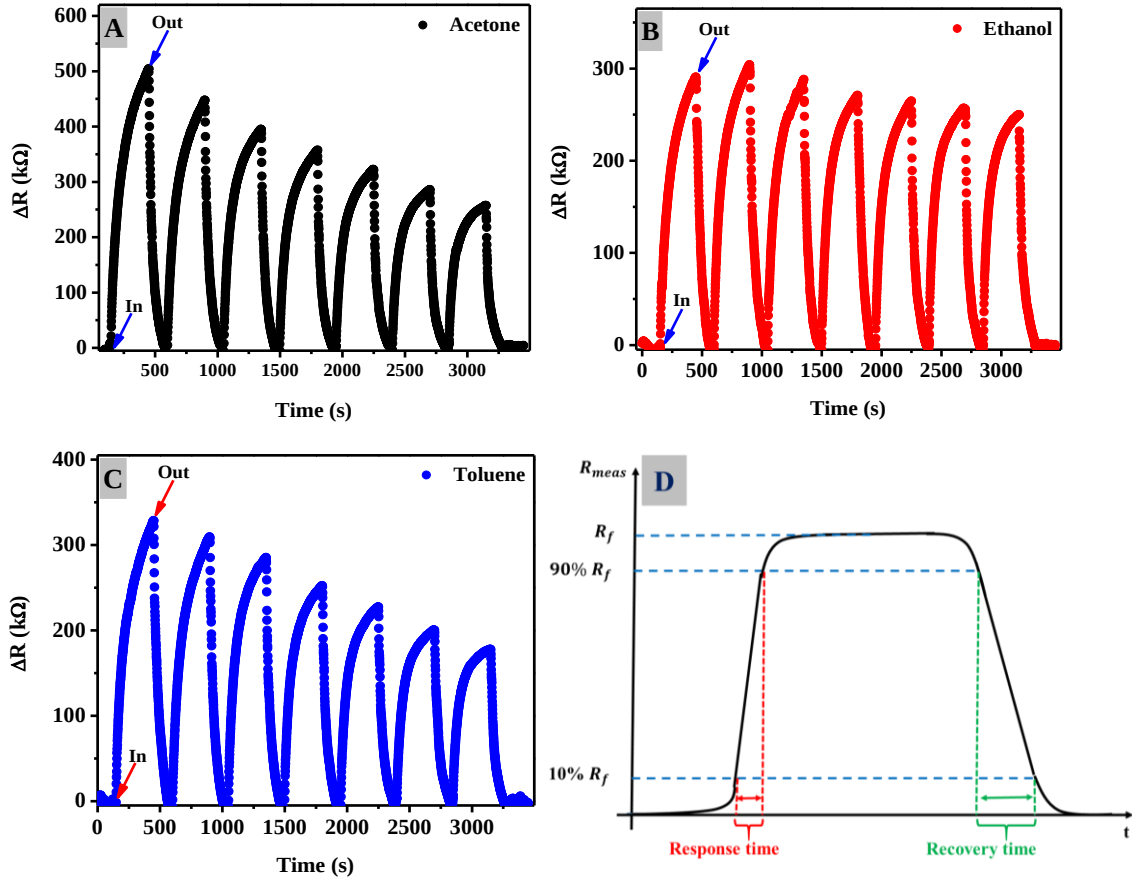


Figure 7.16: Response and recovery time measurement results for an increasing 1 μ L intervals of; (a) acetone, (b) ethanol, (c) toluene and the (d) scheme of the response and recovery time calculations stimulated as a step-function [53, 89].

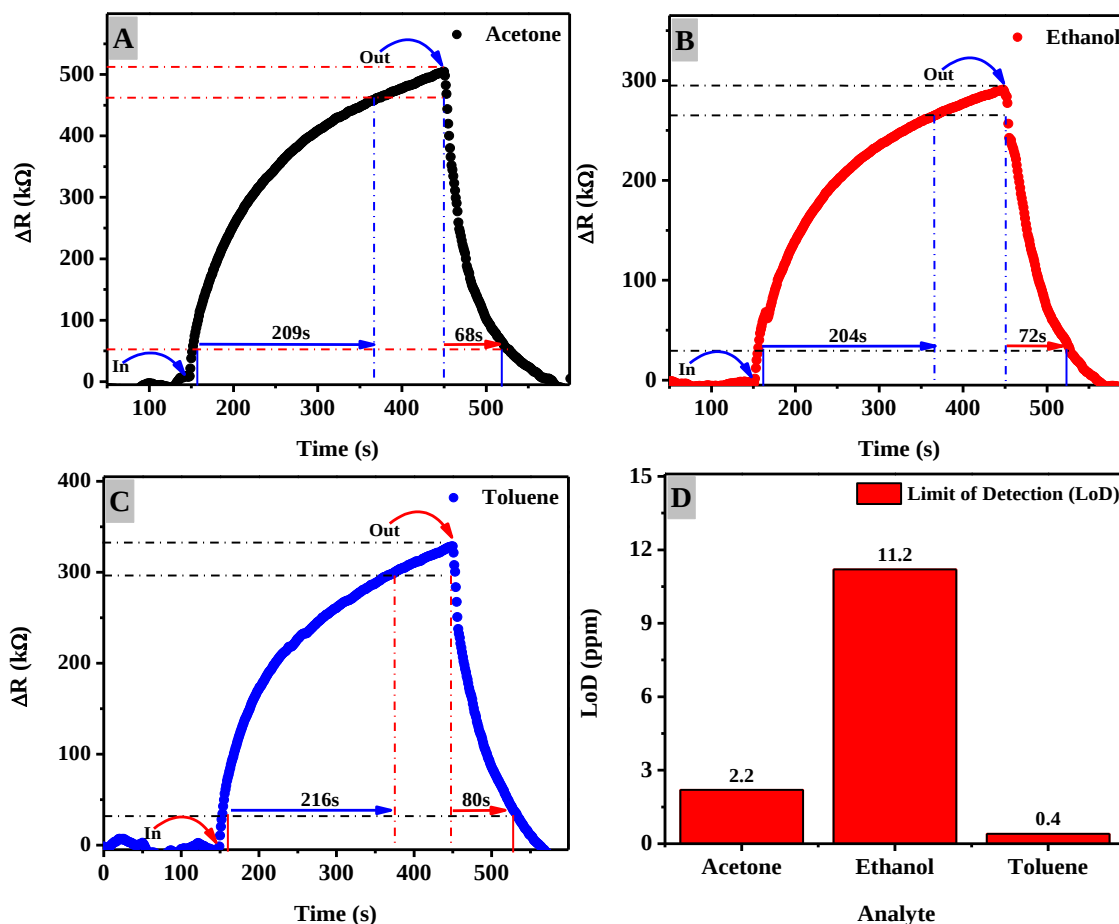


Figure 7.17: The zoomed (between 150s and 600s) response and recovery time measurement results for the first 1 μ L of; (a) acetone, (b) ethanol, (c) toluene and the (d) bar graph that compares the response and recovery times for all analytes.

7.5. Conclusions

In-situ nitrogen doped quasi-spherical CLCNOs with particle sizes of ca. 69.6 ± 3.5 nm can be synthesized using the pyridine as a carbon precursor in flame pyrolysis process. The significance of N-CLCNOs is their unique response towards the detection of acetone, ethanol and toluene which was promoted by the presence of different hetero-atomic species exhibited on their surfaces. This carbonaceous material exhibit structural defects including the presence of nitrogen and oxygen containing groups on their structural surfaces. The presented data indicates that the physicochemical properties of the N-CLCNOs and MONRs influence the response of the fabricated device towards the detection of different analytes at room temperature. The lowest LoD and highest sensitivity obtained in comparison, revealed a good response towards toluene given off by the N-CLCNOs/MONRs/PVP composite based sensor. However, the response was only

observed whenever the three materials (i.e. PVP, CLCNOs and MONRs) were used to form the active sensing composite. It was observed that the sensor can be used at different operating frequencies in order to study its response at frequencies higher than 6.5 kHz. In the other hand, the sensor's dynamic characterization showed that the response and recovery times for detecting the three analytes are slightly different with few seconds. It can be said that the devices behave as reversible systems since both the response and recovery times were obtained for all devices tested. This investigation revealed that the sensor responded faster towards ethanol (204s) in which the recovery time was the second best after taking 72s to recover to its initial sensing state. Thus, it can be said that nitrogen doped CLCNOs exhibit interesting surface properties that are important to tune the gas sensing response depending on the operational conditions of the device. Hence, it can be said that different composites that are based on doped carbon nano-onions can be developed using various shaped metal oxide nanoparticles to improve the devices performance.

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CHAPTER 8

The selective study of response and recovery times of acetone and ammonia room temperature gas sensors fabricated using nitrogen doped carbon nano-onions/manganese oxide nanorods composite

8.1. Introduction

Recently, sensors have become one of the daily used electronic devices to an extent that most people are not aware of their significance in the modern lifestyle. However, sensing devices are important for various living purposes. For example, one type of useful sensor among others is the photosensor which is commonly used to turn light on and off [1-3]. By definition, a chemical sensor is a miniaturized device that is capable of delivering real-time information online following the use of specific compounds and/or ions in complex sensing materials [4]. Its working principle is mainly based on the electrical variation that is introduced in the sensing active layer whenever the targeted gas molecules turn to diffuse or react chemically within the sensing area. Hence, chemical sensors are often used in many applications which include their use in detecting and monitoring toxic and/or flammable gases when they exceed their critical threshold to save the lives of living organisms [5]. During their fabrication, most metal oxides such as zinc oxide (ZnO) are used due to their interesting physicochemical properties that are capable of adsorbing various VOCs (e.g. ethanol) [6-8]. Whenever a metal oxide (MO) is used in a gas sensing system, absorption or desorption of analyte/VOC gas molecules occurs predominantly on its surface active sites. The conductivity of the MO-based sensing material changes when the analyte molecules interact with the sensing material. This phenomenon was first demonstrated by Seiyama *et al.*, in 1962 using ZnO thin film as a sensing layer in which further studies reported on the sensitivity of a sensing material towards molecules of the target analyte (e.g. acetone) in as low as parts per billion (ppb) [9-12].

In fact, MO-based sensors should have a large surface area to be capable of adsorbing enough target analyte molecules as easy as possible on its active sensing surface. The larger surface area

will allow for more measurable response which in turn gives stronger response signals especially at low concentrations of the analyte. However, the semiconducting MO-based sensors still exhibit limitations such as poor selectivity as well as high operating temperatures which are typically within the 300 to 500 °C range [13]. This limitations relies on their working principles which involve chemical oxidizing reaction and alternatively the reducing reactions between oxygen ions and the analyte molecules whereas the analytes molecules have similar reducing reaction energies [13]. Moreover, the high operating temperatures are necessary for generating oxygen ions that are important for the desired redox reactions. Hence, these drawbacks contribute to the issue of power consumption and decrease the device's portability and/or usability. Thus, the unique properties that include high sensing performance sensing, portability, and low power consumption are desired in nanomaterials used in the fabrication of VOCs sensing to give a good device design.

Fortunately, materials such as polymers represent a class of VOCs sensing materials that can work at room temperature. Various polymers exhibit good absorption ability toward different VOC molecules due to their porous and fibrous structures which also provide a larger surface area that allows for the provision of more adsorption sites on the surfaces of the sensing material [14]. They can be used along with MO semiconductors that are widely studied and exploited in gas-sensing devices. These materials can be mainly used in conductometric sensors or chemiresistors in which they can transduce the reaction with the analytes molecules through alteration of electrical resistance [15].

One of the non-conductive polymers that are seldom studied is the polyvinylpyrrolidone (PVP). However, this polymer deserves attention in the application of sensing technology including its use in chemiresistive gas sensing composites due to its ability to control and stabilize the morphology of other nanoparticles (e.g. carbon nanoparticles) in a sensing composite [16]. Moreover, its main functional groups such as carboxyl and nitroxyl groups are also the main contributors to the gas sensing mechanism [17]. With its fascinating physicochemical (e.g. high porosity and larger surface area) properties, the structural flexibility, low costing and low toxic manganese dioxide (MONRs) is among the semiconducting metal oxides that can be applied in gas sensing [18-20]. It can exist in different polymorphs including the; α -, β -, and δ -MONRs which can be derived from the inter-linking chains of MnO_6 octahedron which is its basic structural unit. In most cases, α -MONRs polymorph is used in various applications since it exhibits nanorods structural shape and it can be synthesized using the hydrothermal process [21-22]. The use of semiconducting metal oxides that are stabilized with selective polymers offers the potential of

chemiresistive sensors to detect various VOCs [23-25]. This can arise from the sensitivity of the sensor towards several VOCs, their reduced size and weight, which make them suitable to develop portable instrumentation [26]. Moreover, their reduced size and weight can be achieved by adding lightweight carbon nanomaterial (CNMs) to form enhanced sensing films. Different CNMs such as carbon nanotubes are widely used for fabricating gas sensors [27].

Among a group of carbon nano spherical materials, chain-like carbon nano-onions (CLCNOs) exhibit interesting physicochemical properties such as high electrical conductivity and large surface area [28-30]. They are entirely composed of surface atoms which can facilitate their expected sensitivity toward any adsorbents whenever they are used as the sensing material. Similar to the carbon nanotubes based sensors, the CLCNOs-based chemiresistive sensor can offer significant advantages over conventional metal oxide-based sensor [31]. The advantages include room temperature operation, improved sensitivity as well as easy miniaturization of device fabrication due to their facile synthesis processes [32-36]. Therefore, CLCNOs derived from olive oil can be applied in chemiresistive gas sensors in a MO-based composite with the polymer. In this study discusses a rarely reported topic based on nanocomposite formed with MONRs and PVP mixture that can provide a good active sensing material for purposes of VOCs detection at room temperature. Thus, a composite made of olive oil derived CLCNOs, MONRs and PVP will allow for better adsorption and desorption of oxygen molecules around sensing composite that contains the metal oxide. Moreover, the CLCNOs will further promote charge carriers mobility within the metal oxides based nanocomposite [37]. Thus, a dynamic characteristics (i.e. response and recovery time) study can be conducted using CLCNOs/MONRs/PVP composite as a sensing film. As such, the hypothesis is that the synergistic activity of CLCNOs and MONRs mixed with PVP will allow for fundamental detection of different VOCs (herein; acetone and ammonia in solution) at room temperature through using chemical resistive sensing devices.

8.2. Experimental

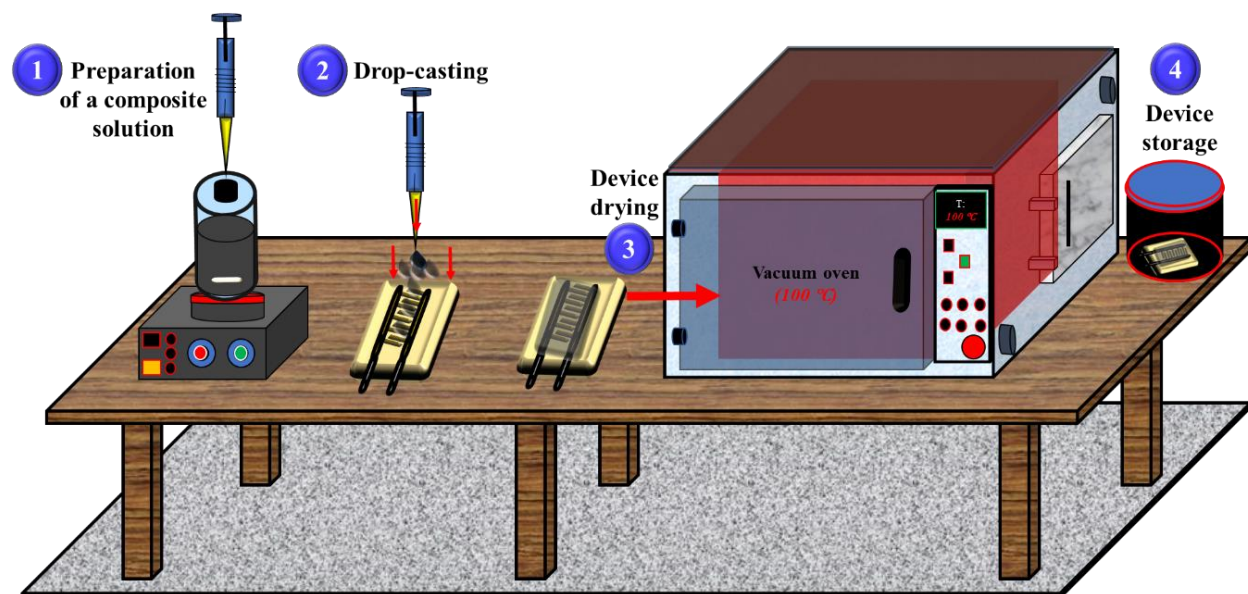
8.2.1. Starting materials and the syntheses of different CLCNOs

Olive oil (Hercules Company, Durban, South Africa) and a fibre glass wick (purchased from a local retailer) were used as received. A polished brass collecting plate and a steel-tube stand (see **Scheme 5.1**) were made in the University of the Witwatersrand Physical Sciences Workshop. Ammonia, argon and compressed air (NH_3 , Ar, and Air) were purchased from Afrox, South Africa. Acetone, air, ammonia solution, ethanol, hexane, manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$),

polyvinylpyrrolidone (PVP), potassium permanganate (KMnO_4) and toluene were also purchased from Merck and were used as received. As discussed in **Section 5.2.2**, the flame pyrolysis method was utilized for synthesizing CLCNOs from olive oil. The chemical vapour deposition method was also employed for ex-situ nitrogen doping using ammonia (NH_3) as the nitrogen source. With the ex-situ doping process, 100 sccm of NH_3 was used as the selected doping source flow rate. Thus, the synthesized materials were labelled as pCLCNOs and N-CLCNOs for pristine CLCNOs (i.e. olive oil derived) and nitrogen doped CLCNOs respectively.

8.2.2. Fabrication and testing of the sensing devices

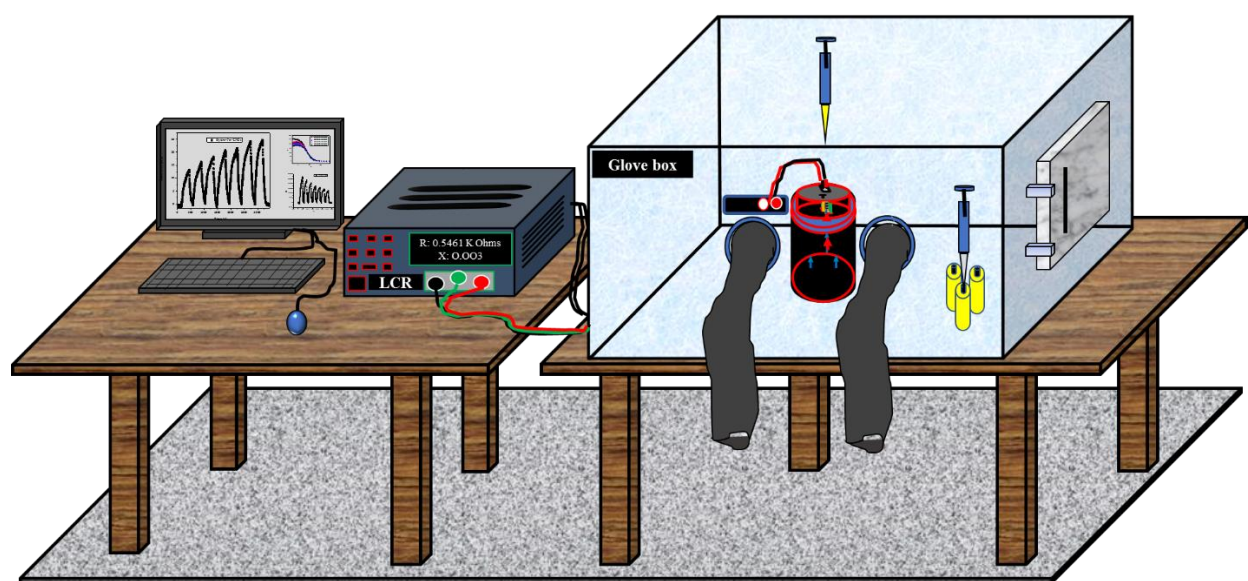
A mixed materials solution (i.e. composite solution) was firstly prepared using pCLCNOs, manganese dioxide (MnO_2 -nanorods (MONRs)), polyvinylpyrrolidone (PVP) and dimethylformamide (DMF). This was also done for preparing the N-CLCNOs based composite solution. Different CLCNOs/MONRs/PVP composites were prepared using a 1:1:3 ratio of pCLCNOs:MONRs:PVP and/or N-CLCNOs:MONRs:PVP was added to 3 mL of DMF. Every mixture was stirred for 12 h at room temperature followed by sonication for 1 h to obtain a homogeneous suspension.



Scheme 8.1: Steps followed during each gas sensing device preparations.

The inter-digitated electrodes (IDEs) used for the device fabrication were cleaned following a standard procedure as discussed in **Section 5.2.4**. As shown in **Scheme 8.1**, the composite solution

was drop casted onto the dry IDEs. A micropipette was used to drop cast 10 μL of each composite solution onto different IDEs to give pCLCNOs- and N-CLCNOs-based sensing devices. The resulting sensors were vacuum dried at 100 $^{\circ}\text{C}$ for 30 minutes, kept in a desiccator and labelled as pS and N_S respectively. The fabricated sensors were tested using the Agilent 4284A Precision LCR meter instrument. All tests were conducted in a sealed glove box environment in which the relative humidity (RH) was maintained at 27% (see **Scheme 8.2** and **Figure S8.1**). The RH below 30% was constantly monitored by using a constant flow of nitrogen at 300 sccm that was considered as a diluting purging gas used to limit and/or reduce high (i.e. RH: $>30\%$) moisture contents that can greatly affect the analyte detection at 25 $^{\circ}\text{C}$.



Scheme 8.2: The LCR meter and glove box set-up used during the static characterization.

The resistance as a function of time measurements was conducted after selecting the best working frequency (i.e. 10 kHz) following the signal-to-noise ratio (SNR) results. All measurements were conducted as described in **Section 7.2.4** [38].

8.3. Results and discussions

8.3.1. Electrochemical tests for detecting VOCs: Chemiresistance measurements of the pCLCNOs and N-CLCNOs sensing device

A discuss based on the static characterization of gas sensing devices aimed at detecting volatile organic chemicals is give herein [39, 40]. The response and recovery times were studied by investigating the chemiresistive behavior of pCLCNOs/MONRs/PVP and N-CLCNOs/MONRs/PVP composite during the detection of acetone and ammonia. However, it is always important to investigate the best operating frequency of the sensing device using the highest signal to noise ratio (SNR) since the change in resistance of these devices does not only depend on the analyte's concentration. Thus, determining the highest SNR allows for static characterization (i.e. response and recovery times) using the optimal frequency. Moreover, quantities that slowly changes with time such as the linearity and sensitivity of the devices can be measured at constant time intervals. Notably, the SNR plot indicates that the prepared sensing devices using the given IDE has the highest SNR at 10 kHz in both cases as shown in **Figure 8.1(a) and (b)**.

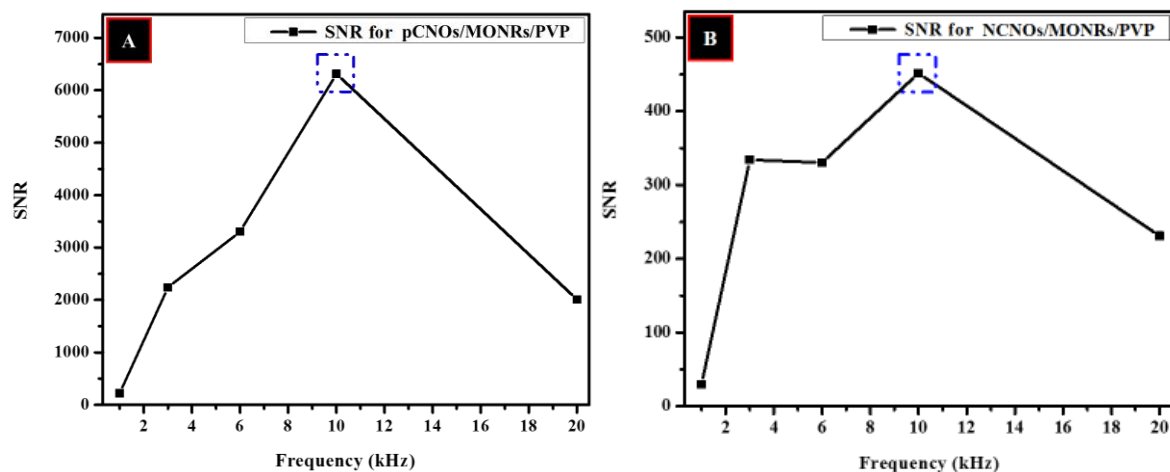


Figure 8.1: SNR plot representing sensor's highest response at 10 kHz for; (a) pCLCNOs/MONRs/PVP-based sensor and (b) N-CLCNOs/MONRs/PVP-based sensor.

In this case, MONRs has been used to make the sensing composite which is best known to offers the n-type metal oxide semiconducting properties. The use of MONRs provides negative charge carriers as the majority charge carriers in the sensing composite. The presence of major negative charge carriers results in an increased conductivity which occurs in the presence of a reducing gas [41]. Alternatively, a decrease in conductivity can be observed whenever an oxidizing gas is detected by the sensing material. Therefore, with MONRs contained in the sensing composite, it can be seen that the resistance of the sensors either decreases or increases as the concentration of acetone or ammonia increases whenever 10 kHz is used during chemiresistance measurements (see **Figure 8.2(a-d)**).

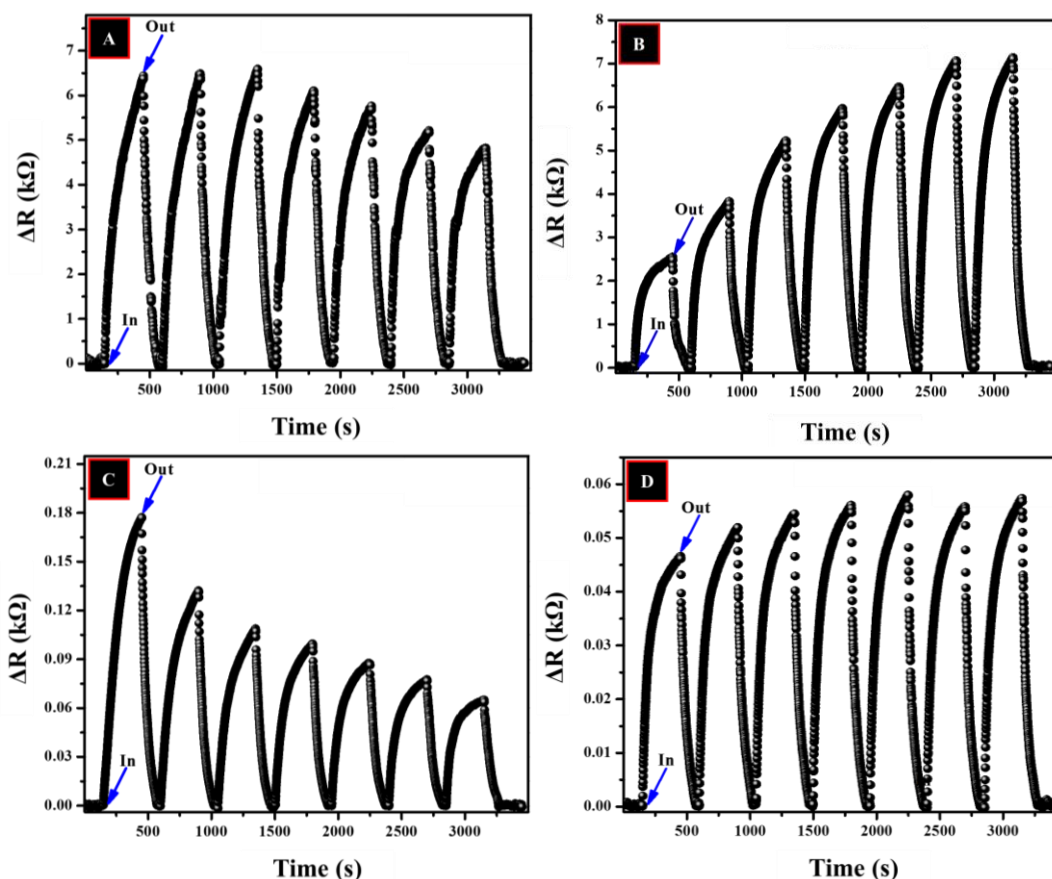


Figure 8.2: Response and recovery time measurement results for detection of; (a) acetone using pCLCNs/MONRs/PVP, (b) ammonia solution using pCLCNs/MONRs/PVP, (c) acetone using N-CLCNs/MONRs/PVP and (d) ammonia using N-CLCNs/MONRs/PVP at an increasing 1 μ L intervals.

The observed trend suggests that the detected analytes exhibit properties (e.g. functional groups) that facilitates molecular interaction with the MONRs which were used to make the active sensing materials for different detectors. Hence, the results shown in **Figure 8.2** presents alternating response towards acetone and ammonia. Interestingly, it was observed that whenever pCLCNOs/MONRs/PVP or N-CLCNOs/MONRs/PVP is used as the sensing material, the relative resistance decreases when acetone is detected in both cases. Alternatively, the relative resistance increases during the detection of ammonia. Thus, the ammonia solution oxidizes the surface of both sensing composites as seen by an increased resistance. This similar behaviour given by both composites towards each analyte suggests that there is a slight difference provided by doping CLCNOs with nitrogen. Thus, it can be suggested that acetone facilitated the molecular interactions between the two different composites in which it has presented electron donating effects since the resistance decreased in both cases [41-43]. On the other hand, ammonia molecules are also considered to be electron donors considering the available electrons (lone pair(s)) carried by the nitrogen atom(s) but it was observed that both sensor's response suggests that during its detection, a decreases the charge carrier mobility takes place. This can be ascribed to its similar dipole–dipole interactions with different carbon-based sensing material surface in which its chemical interactions with the sensing composites are mainly controlled by the type of active attachment sites on the sensing material surfaces. As seen in the case of acetone detection, N-CLCNOs/MONRs/PVP composite presented a good linear behaviour as compared to its counterpart (i.e. pCLCNOs/MONR/PVP composite) (see **Figure 8.3**). However, a good linear behaviour was observed for pCLCNOs/MONRs/PVP whenever ammonia was detected as shown in **Figure 8.3**.

Two time factors were further investigated, namely the; (1) response time and (2) recovery time following the positive response of the gas sensors towards acetone and ammonia. The results are shown in **Figure 8.2** and **8.4(a-d)** reveal that all analytes interact with the sensing material as shown by the change in resistance with increasing time. With the results in **Figure 8.4(a-d)** and **8.5**, it is evident that the $_NS$ (i.e. N-CLCNOs/MONRs/PVP-based) sensor responds faster towards acetone and ammonia as compared to its counterparts (i.e. $_pS$). The $_NS$ sensor takes about 197s and 175s to respond towards acetone and ammonia respectively. On the other hand, $_pS$ sensor takes about 234s and 205s to respond towards acetone and ammonia. However, the sensors have similar recovery durations since $_pS$ takes about 75s and 78s to recover after detecting acetone and

ammonia whereas N_S takes about 79s and 84s respectively. In each sensor's case, the analyte molecules sieve through different sensing material and rapidly occupy the active sites in which Knudse diffusion effects take place during the chemical interaction [44]. The faster response duration for N_S towards both analytes is ascribed to increased density of negative charge carriers as well as possible proton hopping within the sensing composite. Moreover, the structural defects on the carbonaceous material also provided defects sites induced by doping which could have also acted as analytes attachment sites for the improved response as compared to pS. It was noticed that the saturation or steady-state of the sensor occurred for less than 100s for all analytes.

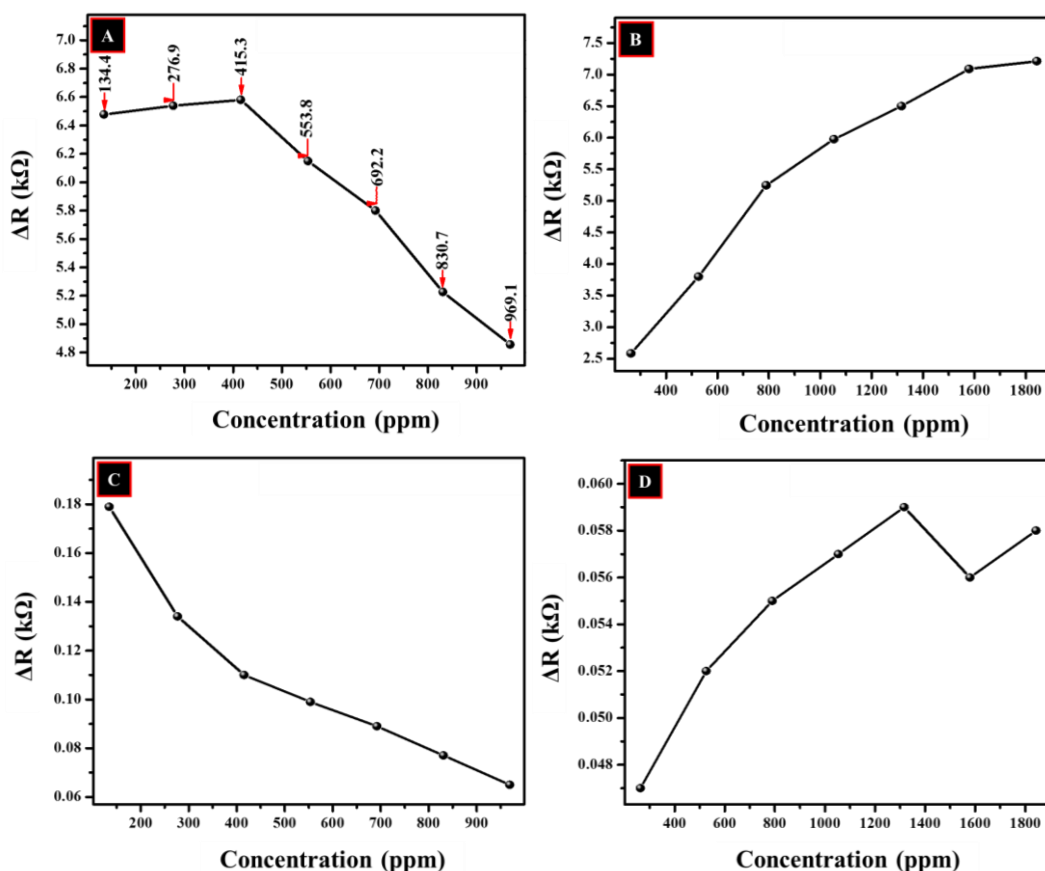


Figure 8.3: Plots that indicate the sensor's linearity obtained following the detection of; (a) acetone using pCLCNOs/MONRs/PVP, (b) ammonia using pCLCNOs/MONRs/PVP, (c) acetone using N-CLCNOs/MONRs/PVP and (d) ammonia using N-CLCNOs/MONRs/PVP.

Following the sensors response results, it is evident that both sensors present the n-type behavior during the detection of acetone as shown by a decrease in relative resistance with increasing

concentrations of both analytes. Whereas in the case of ammonia detection, an increase in relative resistance with increasing concentrations of both analytes suggesting a p-type gas sensing behavior was observed [45].

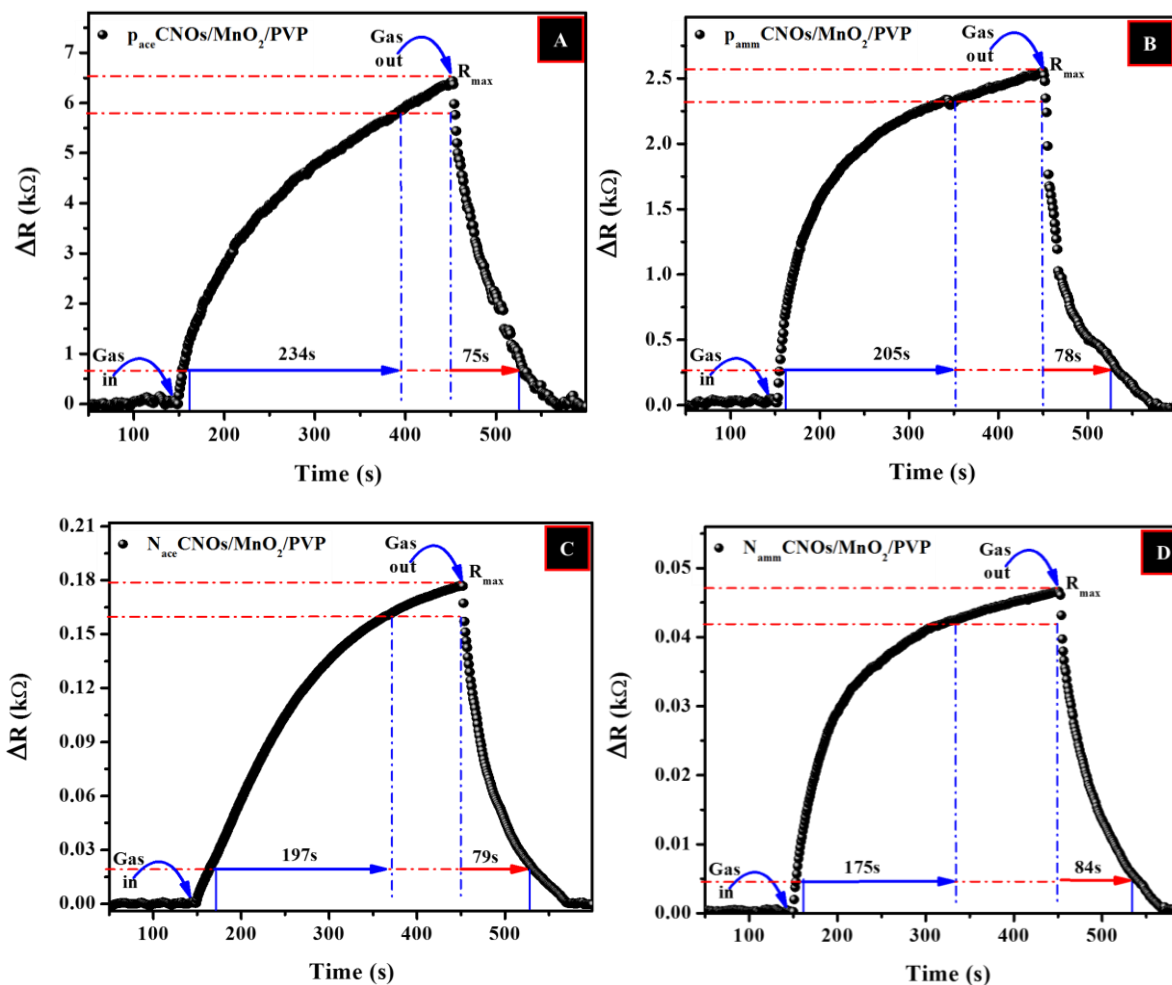
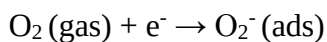
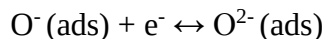
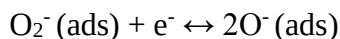
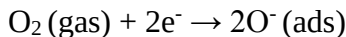


Figure 8.4: Zoomed (between 150s and 600s) response and recovery time measurement results for detection of ; (a) acetone using pCLCNs/MONRs/PVP, (b) ammonia using pCLCNs/MONRs/PVP, (c) acetone N-CLCNs/MONRs/PVP, and (d) ammonia using N-CLCNs/MONRs/PVP at the first 1 μ L injection.

As discussed in **Section 6.5.1**, it is possible for oxygen species such as O^{2-} to exist on the surface of the sensing composite. This type of species (i.e. oxo) can dissociate after capturing an additional electron from a donor to form other oxygen species such as O^- (oxide) as described in the reaction equations below [46]:-



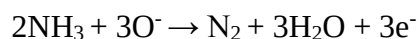
or



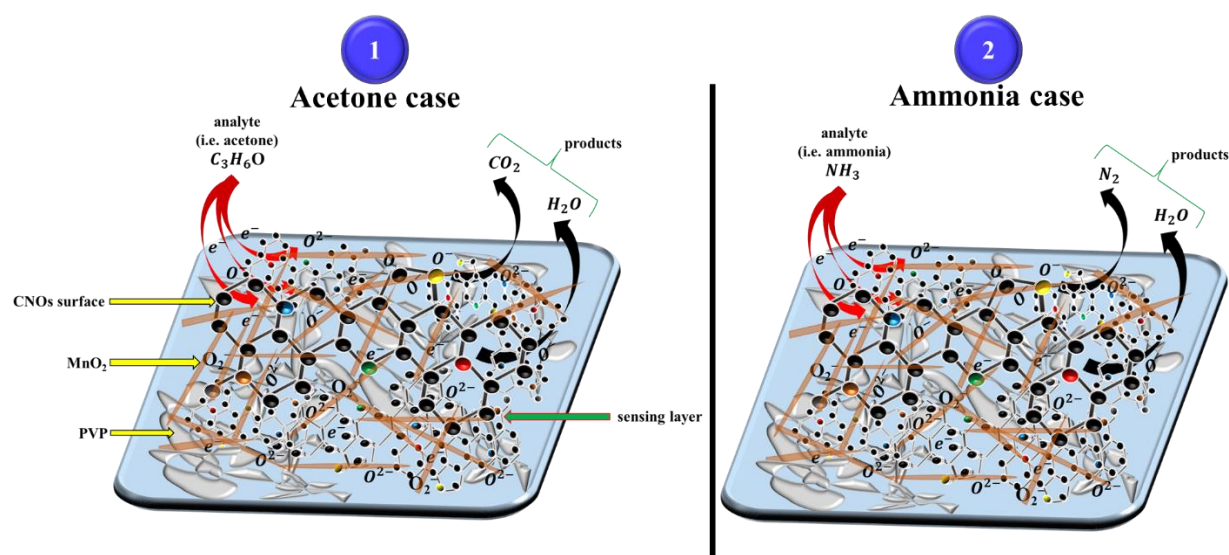
Therefore, the oxidation of acetone molecules at the surface of the sensing materials follows the reaction mechanism below [46-48]:-



Additionally, in the case of ammonia, a p-type sensing behavior was observed and it can be attributed to the presence of electron lone pair that could have also provided a stronger electron accepting interaction with the adsorbed oxygen ions on the surface of the sensing material [49]. It can also be suggested that the trapped electrons on the surface of the sensing material were reverted during the redox reaction that occurs during the interaction [50-52]. For example, NH_3 molecules can interact with carboxylic and/or nitroxyl groups provided by the carbonaceous material on the surface of the MONRs-based sensing composite with possible formation of ammonium salts (NH_4^+) that can promote electron withdrawing effects resulting in disruption of charge carrier mobility (i.e. increase in resistance). Moreover, NH_3 molecules can dissolve during the physical adsorption process [53-55]. Hence, the following reaction mechanism can be suggested for the fundamental reaction that takes place between ammonia and different CLCNOs-based sensing materials [56].



During the detection of ammonia, an additional electron can be captured by the O^{2-} species resulting in the generation of O^- . The electron donating groups can be from the OH^- species generated from the water molecules (H_2O) that dissociate into two ions (i.e. H^+ and OH^-) since ammonia solution was used in this study.



Scheme 8.3: CLCNOs-based sensing surface drawings for the proposed acetone and ammonia sensing mechanism.

This observation was then followed by determinations of the sensitivity of the sensor towards both analytes. By assuming the sensors linear behavior, the change in each sensor's response per concentration unit of the analyte was determined as the sensor's sensitivity (S) using the slope of a calibration curve.

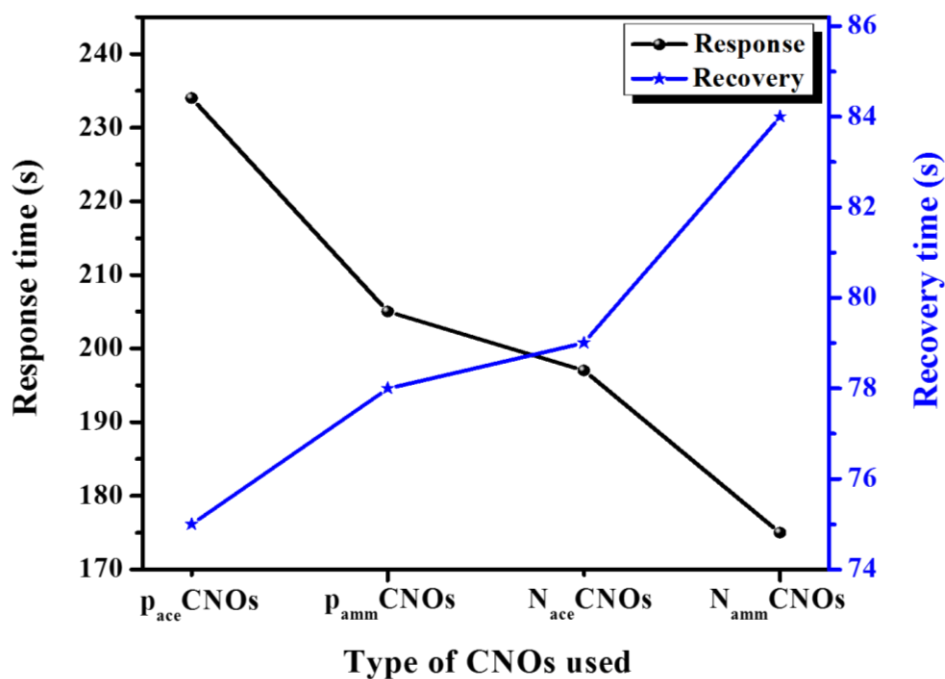


Figure 8.5: Comparison plots for the sensors' response and recovery times.

The results in **Figure 8.6** and **8.7** reveals that there is a significant difference in terms of the sensitivity towards both analytes whenever the pCLCNOs/MONRs/PVP and N-CLCNOs/MONRs/PVP composites are used. Notably, pS is highly sensitive towards detecting both analytes as compared to _NS. pS presented the highest sensitivity towards acetone (i.e. $pS_{\text{acetone}}: 2.12 \times 10^{-3} \text{ ppm}^{-1}$) followed by that towards ammonia detection given as $pS_{\text{ammonia}}: 1.92 \times 10^{-3} \text{ ppm}^{-1}$.

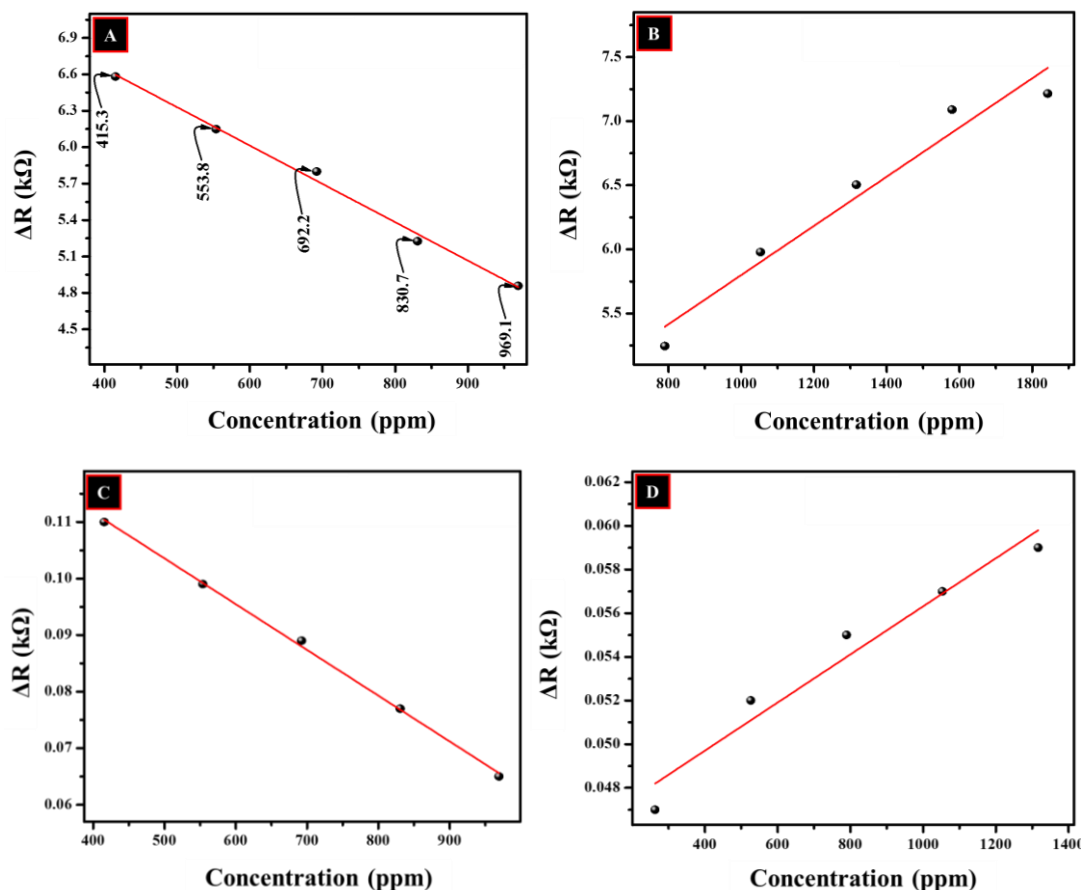


Figure 8.6: Plots shows sensor's sensitivities towards the detection of; (a) acetone using pCLCNOs/MONRs/PVP, (b) ammonia using pCLCNOs/MONRs/PVP, (c) acetone N-CLCNOs/MONRs/PVP and the (d) ammonia using N-CLCNOs/MONRs/PVP.

In the case of _NS, a similar sensitivity trend was noticed in terms of detecting the two analytes whereby the highest sensitivity was observed towards acetone (i.e. $N_{\text{S}_{\text{acetone}}}: 8.09 \times 10^{-5} \text{ ppm}^{-1}$) followed by that towards ammonia detection given as $N_{\text{S}_{\text{ammonia}}}: 1.10 \times 10^{-5} \text{ ppm}^{-1}$. Hence, the decreasing order of sensitivities towards acetone was obtained $pS_{\text{acetone}}: 2.12 \times 10^{-3} \text{ ppm}^{-1} > N_{\text{S}_{\text{acetone}}}$.

$8.09 \times 10^{-5} \text{ ppm}^{-1}$ and that towards ammonia is $pS_{\text{ammonia}}: 1.92 \times 10^{-3} \text{ ppm}^{-1} > nS_{\text{ammonia}}: 1.10 \times 10^{-5} \text{ ppm}^{-1}$ (see **Figure 8.7**). This observation is attributed to the defects densities of the composites which facilitates the molecular interactions between the analytes and the sensing materials. For example, when pCLCNOs are used in the composite together with MONRs, the oxygen species that are available on the surfaces of the composite easily provide reactive sites for the decomposition and detection of a carboxylic or nitrogen group carrying molecules of acetone or ammonia. However, in the case of N-CLCNOs/MONRs/PVP-based sensor, there exist multiple active sites such as the nitroxyl groups as well as the oxygen sites from N-CLCNOs and MONRs which delays the identification of both analytes as compared to a pCLCNOs/MONRs/PVP-based sensor through side reactions that occur on the sensing material's surfaces.

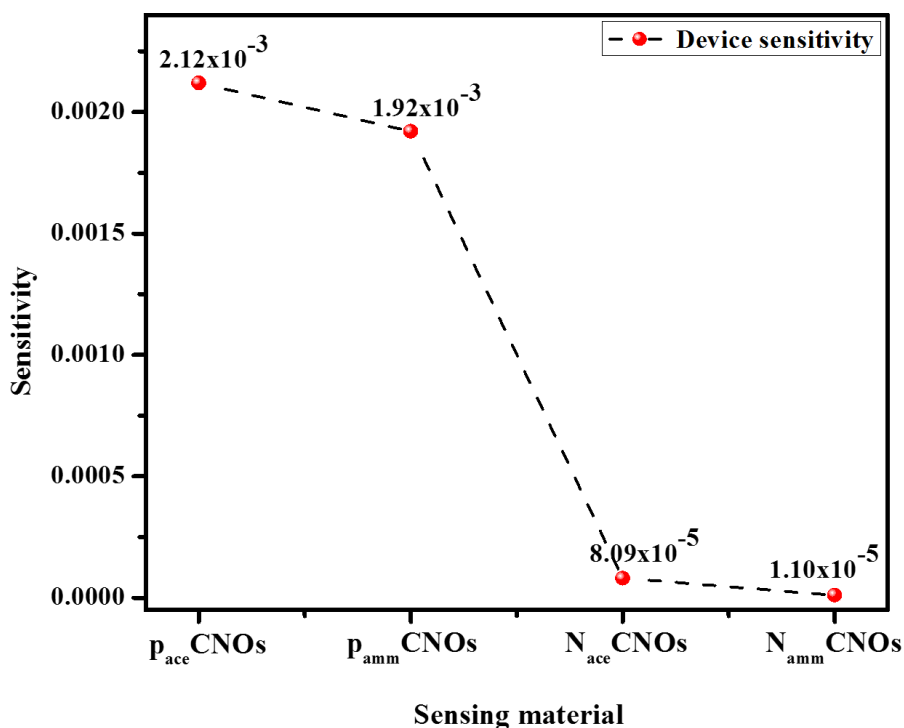


Figure 8.7: Sensitivity comparison plot for detection of acetone and ammonia using two different composites that are composed of pCLCNOs and N-CLCNOs.

8.4. Conclusions

In this study, it was realized the significance of carbonaceous material that exhibit structural defects including the presence of nitrogen containing groups on their structural surfaces. The obtained data mostly indicated that there exists a physical interaction between pCLCNOs or N-

CLCNOs with MONRs along with PVP which influence the response of the fabricated gas sensing devices used towards the detection of acetone and ammonia at room temperature. It was also discovered and learned that nitrogen doping CLCNOs with nitrogen improves the MONRs-based sensing composite's response time towards acetone and ammonia. However, it does not improve the sensor's sensitivity towards both analytes. Moreover, observations were made which showed that the sensors present an n- or p-type sensing behaviour depending on the chemical interaction that takes place between the analytes molecules and the sensing composite. Thus, it can be suggested that there is great potential to improve the chemical sensing properties using different composites based on other hetero-atoms decorated CLCNOs (e.g. boron doped CLCNOs), and various shaped metal oxide nanoparticles (e.g. TiO_2) to understand the sensing properties of carbon to MO-based composites.

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CHAPTER 9

The study of functionalized carbon nano-onions and their metal oxide-containing composite for application in chemiresistive gas sensors

9.1. Introduction

Dense or solid chain-like carbon nano-onions (CLCNOs) are amongst the group of carbon nanoparticles that exhibit fascinating physical and chemical properties [1-12]. This unique type of nanomaterial can be synthesized using different methods including the conversion of carbon dioxide (CO_2) by the electrolytic method as well as the flame pyrolysis process using various liquids [13-16]. Commonly, CLCNOs exhibit small, high electrical conductivity, easy solvent dispersion, smaller (<100 nm) particles diameter and they are zero dimensional (0-D) structured nanoparticulate material. As compared to 1-D (e.g. nanotubes) and 2-D (e.g. graphene), CLCNOs are made of concentric shells of graphitic carbon atoms which form quasi-spherical nanoparticles with the number of shells depending on the synthesis method [17, 18]. Hence they are referred to as multi-layered carbon nano-onions as they have a structural architecture that is similar to that of an onion (see **Scheme 9.1**).



Scheme 9.1: The architectural structural model of CNO that exhibit multiple and concentric graphitic layers [19].

Lately, several catalyst-free methods make use of combustible hydrocarbons such as diesel and petrol as carbon sources to form CLCNOs in the gram scale [16, 20, 21]. This method can be considered for its simplicity and large production of CLCNOs such that they can be explored in various applications (e.g. power backup devices and solar cells) [22, 23]. However, they commonly display poor solubility in both aqueous and organic solvents in which limits their applications and exploration due to the aggregation of nanoparticles caused by strong intermolecular interactions such as Van der Waals forces [24]. Thus, to overcome this drawback, the surfaces of CLCNOs can also be functionalized with various functional groups (e.g. hydroxyl groups) [25]. However, most carbon nanomaterials such as carbon nanotubes are functionalized with oxygen-carrying groups using acid-base methods [26]. Thus to avoid these harsh functionalization conditions, hydrogen peroxide can be used instead of acid-base solutions [27-29].

This study reports on functionalized CLCNOs (f-CLCNOs) through their oxidation process using hydrogen peroxide to promote the use of highly oxidized quasi-spherical nanoparticles. However, the f-CLCNOs will be used mainly in manganese dioxide (MnO_2) containing composite. The selective use of MONRs originates from the fact that it has never been explored as a carbon-based composite for its application in gas sensors to detect toxic volatile organic chemicals (VOCs). The discussion herein, report on the exploration of f-CLCNOs/MONRs based composite in which a non-conductive polymer (i.e. polyvinylpyrrolidone (PVP)) is used as a stabilizing agent for detection of VOCs at room temperature. As reported by Okechukwu *et al.*, and Olifant GE *et al.*, the three material based composite shows better sensing response of various analytes at room temperature [30, 31]. Hence, the dynamic (e.g. response and recovery times) and static (signal to noise and precise sensitivity) characteristics of the chemiresistive VOC detecting devices were investigated to reveal the potential of the three nanomaterials based composite in the field of gas sensing [32, 33]. Thus, this study gives a first time discussions based on the exploration of detecting acetone, ethanol, chloroform and toluene using three nanomaterial-based composites (i.e. f-CLCNOs/MONRs/PVP) as an active sensing layer.

9.2. Experimental

9.2.1. Starting materials

Olive oil (Hercules Company, Durban, South Africa) and a fibre-glass wick (purchased from a local retailer) were used as received. A polished brass collecting plate and a steel-tube stand (refer to **Scheme 5.1** in **Chapter 5**) designed with a circular shaped air-flame controlling ring were built in the University of the Witwatersrand physical sciences workshop. The compressed air was purchased from Afrox (South African company). Acetone, air, chloroform, ethanol, hexane, hydrogen peroxide (H_2O_2), manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), polyvinylpyrrolidone (PVP), potassium permanganate (KMnO_4) and toluene were also purchased from Merck and were used as received.

9.2.2. Synthesis of f-CLCNOs using olive oil derived CLCNOs metal oxide nanorods

As discussed in **Chapter 5** in **Section 5.2**, olive oil was used to synthesize CLCNOs which were later treated with 50 mL of 50% H_2O_2 under refluxing conditions. Typically, the as-prepared CLCNOs were cleaned by hexane through Soxhlet extraction. About 1.5 g of cleaned CLCNOs were taken into a round bottom flask containing H_2O_2 to form a homogenous mixture. Thereafter, the mixture was stirred at 80 °C for 12 hours aiming at introducing more oxygen-carrying functional groups (e.g. carboxylic groups (COO)) on CLCNOs surfaces. After completion of refluxing, the obtained product deemed as f-CLCNOs containing solution was filtered and washed several times with deionized water. The resultant solid dark solid product was slowly dried for 12 hours in an oven at 100 °C overnight to obtain f-CLCNOs black-powdered product. In addition, manganese oxide nanorods (MONRs) were synthesized using a method previously reported by Wang *et al.*, without any modification as described in **Section 5.2.3** [34].

9.2.3. Fabrication of the sensing device using f-CLCNOs in the sensing composite and testing

The mixed materials solution (i.e. composite solution) was prepared using f-CLCNOs, manganese dioxide (i.e. MONRs), polyvinylpyrrolidone (PVP) and dimethylformamide (DMF). This was followed by all other post-steps similar to those described in **Section 7.2.4**. The resulting sensor was and labelled as f-S since the sensing material was composed with f-CLCNOs respectively.

9.3. Techniques used to characterize the nanomaterials used to form the sensing material

The structural morphology and characteristics of the f-CLCNOs were ascertained by transmission electron microscopy (TEM) using a Tecnai G2 30ST operating at 200 kV. The quality and structural properties of CNOs (supported on a silicon wafer (2 mg sample holder)) and its metal oxide composite were investigated using a Jobin-Yvon T64000 Ultraviolet (UV) LabRam HR-micro Raman spectrometer with an Olympus BX41 microscope, that makes use of a liquid nitrogen-cooled charge-coupled device detector working at an excitation wavelength of 514.5 nm at room temperature. A Bruker D2 Phaser XRD that uses Cu-K α irradiation and operated at 30 kV with the X-ray tube at the current of 30 mA over a $10^\circ \leq 2\theta \leq 90^\circ$ scanning range was used to analyse the crystallographic nature of the CLCNOs based samples.

The thermal stability of CLCNOs (10 mg) was monitored using a Perkin Elmer 6000 thermogravimetric analyser. A Micromeritics Tristar 3000 surface area and porosity analyser were used to determine the surface area and pore volume of CLCNOs (200 mg). Furthermore, the elemental composition of CLCNOs was achieved using two different techniques; (1) the FEI Nova Nanolab 600 FIB-SEM instrument, as well as the FEI Quanta 450 FEG-SEM coupled with the energy dispersive spectroscopy (EDS) detector, was used to determine the structural morphology of CLCNOs and their surface elemental composition respectively, (2) the Physical Electronics Quantum 2000 X-ray photoelectron spectroscopy (XPS), that uses a monochromatic Al K α source operated at 1486.7 eV.

9.4. Results and discussions

9.4.1. Structural morphology and elemental or surface functional groups analysis of f-CLCNOs

The low magnification TEM micrograph in **Figure 9.1** revealed that the f-CLCNOs exhibited dense or solid quasi-spherical shapes with particle sizes of ca. 55 ± 3 nm (also see **Figure 9.2**). The nanoparticles formed conglomerates that are mainly promoted by Van der Waals forces. The conglomeration lead to chain-like connected quasi-spherical nanoparticles that are comprised of

closed cages as seen in **Figure 9.1(b)**. Similar results were obtained by Panda *et al.*, as well as Singh *et al.*, [35, 36].

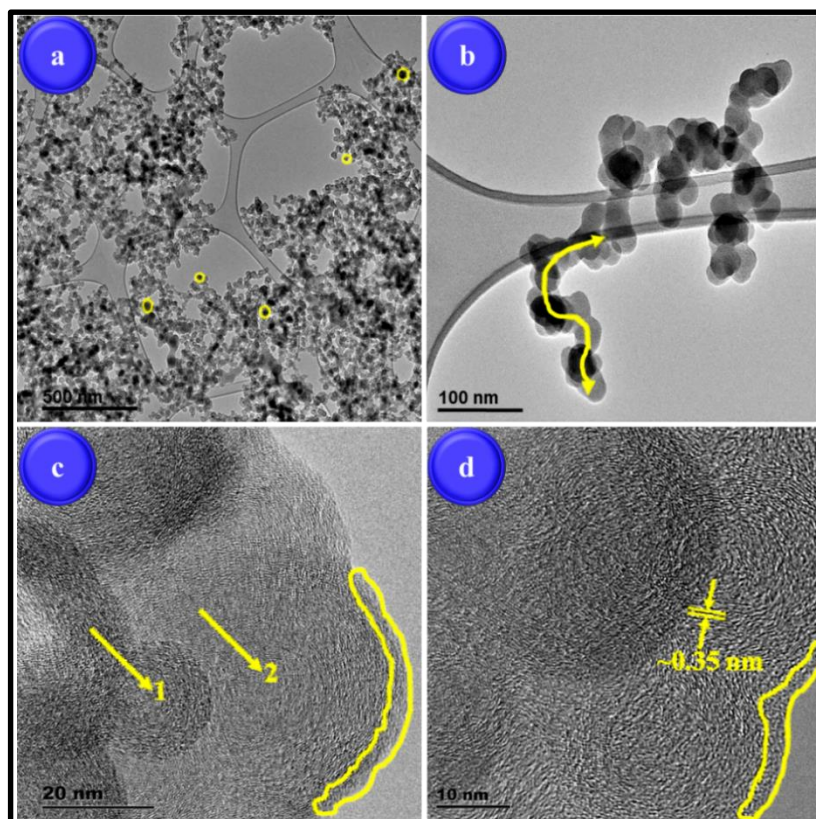


Figure 9.1: Microscopy micrographs of f-CLCNOs; (a) particle sizes that are <100 nm , (b) chain-like connections, (c) multiple stacked cores in different regions, and (d) short range ordered layering with inter-layer spacing.

This observation confirms that the produced material is made of chain-like nanoparticles. **Figure 9.1(c)** reveals that the produced CLCNOs exhibit concentric turbostratic shells with a continuous radially arranged morphology. Hence, the CLCNOs have short-range ordered multiple concentric layers with the inter-layer or lattice fringe spacing of ca. 0.35 nm which indicates the presence of disordered graphitic carbon shells as shown in **Figure 9.1(d)** [37]. This is ascribed to the type of radicals that facilitate the growth process of every particle during the synthesis. Moreover, with a different type of radicals facilitating the particles growth, it was evident that f-CLCNOs have multiple cores as well as different multi-layered regions as indicated arrows and highlighted region in **Figure 9.1(c)** and **Figure 9.1(d)** respectively. Thus, it can be confirmed that treating CNOs with H_2O_2 during the functionalization process did not destroy their morphology. However, f-CLCNOs

retained the short-range ordering of multi-layers similar to those reported in the literature with possible increase in defect sites due to the post-introduction of surface functional groups (see **Figure 9.1(d)**) [38].

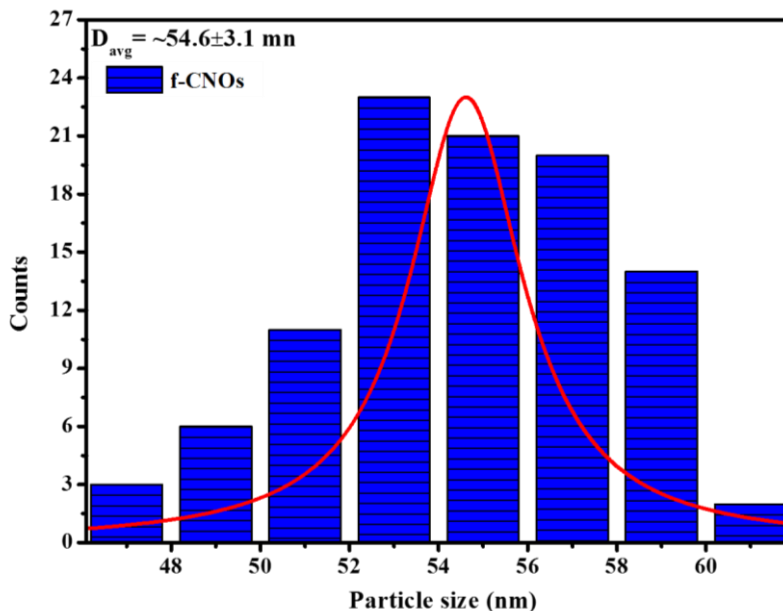


Figure 9.2: Particle sizes distribution obtained from the low magnification TEM micrographs.

Furthermore, the EDS was used to investigate the major atomic contributors on the f-CLCNOs surfaces. The obtained energy dispersive (EDX) spectrum revealed that the f-CLCNOs are mainly composed of elemental carbon and oxygen as shown in **Figure 9.3**. However, it is important to mention that the presented carbon peak (i.e. > 80% of C) is not only from f-CLCNOs but also from the SEM carbon tape on which the sample was deposited which is the component that cannot be avoided when using SEM-energy dispersive spectroscopy technique.

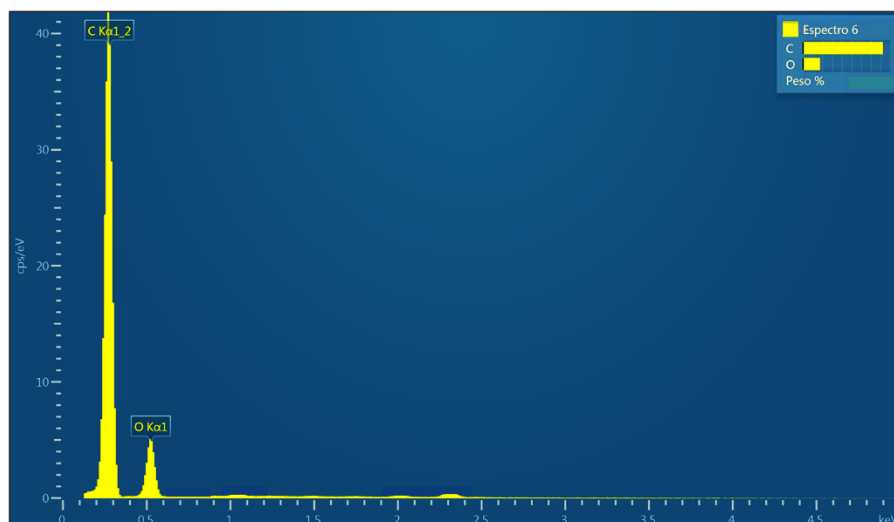


Figure 9.3: EDX spectrum that presents the presence of carbon and oxygen in f-CLCNOs.

To further understand the type of surface functional groups on f-CLCNOs, FTIR technique was used following the EDS results. The FTIR spectrum of f-CLCNOs is presented in **Figure 9.4** and it indicates that there exist several peaks that represent multiple organic functional groups. The broader peak between 3600 and 3000 cm^{-1} is attributed to the presence of hydroxyl groups (O-H) stretching modes [39-42]. Interestingly, the spectrum shows that f-CLCNOs exhibit C-H asymmetric and symmetric stretching vibration modes including C-C stretching vibration modes indicated by the sharp peak around 2900 cm^{-1} as well as the broader peak around 2650 cm^{-1} [43, 44]. This also involved four prominent peaks between 2500 and 1850 cm^{-1} . These results also suggest the presence of aliphatic hydrocarbons which can be within the f-CLCNOs structural matrix [45]. Notably, the broader peak that appeared between 2500 and 2220 cm^{-1} can also accommodate a peak that is ascribed to carbon dioxide (CO_2). The CO_2 presence can be as a result of being entrapped molecules in f-CLCNOs since is one of the pyrolysis (i.e. combustion) by-products entrapped [46]. The presence of carboxyl groups (e.g. C=O) in the structural matrix of f-CLCNOs can be confirmed by the two peaks that stretched between 1760 and 1500 cm^{-1} . The presence of aromatic rings bonded to carboxylic acid groups formed by oxidation of hydroxyl groups that are associated with C-C bond cleavage allows for the presence of carboxyl groups [45, 47].

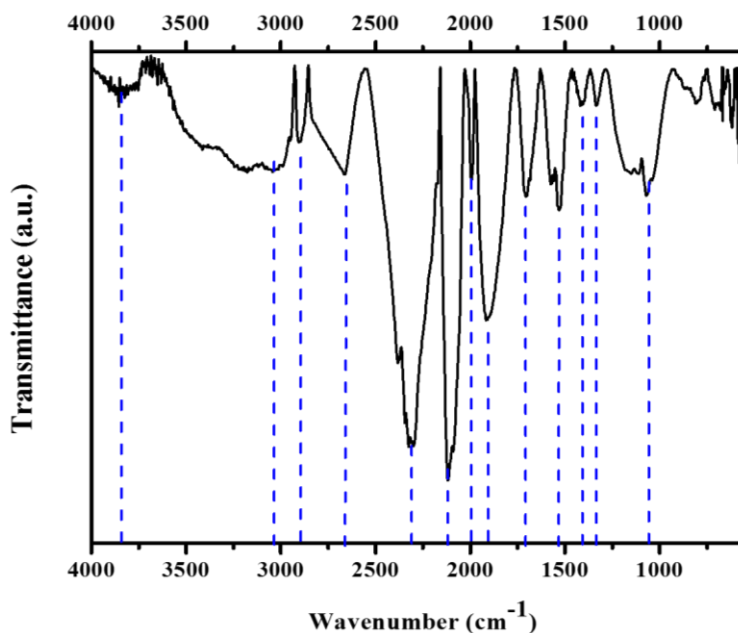


Figure 9.4: FTIR spectrum of f-CLCNOs revealing different surface functional groups.

Moreover, f-CLCNOs exhibit other functional groups such as =C-C= and C-C presented by multiple peaks appearing around 1480, 1415 and 750 cm^{-1} that are attributed to the bending or deformation type of vibration modes [48, 49]. This also involves the broader peaks between 1250 and 1000 cm^{-1} that additionally indicates the presence of carboxylic groups in the structural matrix of f-CLCNOs [50].

To further support the FTIR results about functional groups, X-ray photoelectron spectroscopy was also used to study the type of carbon and oxygen configurations in f-CLCNOs. As shown in **Figure 9.5**, the XPS survey scan reveals that f-CLCNOs exhibit various carbon and oxygen atomic arrangements in the structural matrix which can form groups such as the carboxylic acid groups [51, 52].

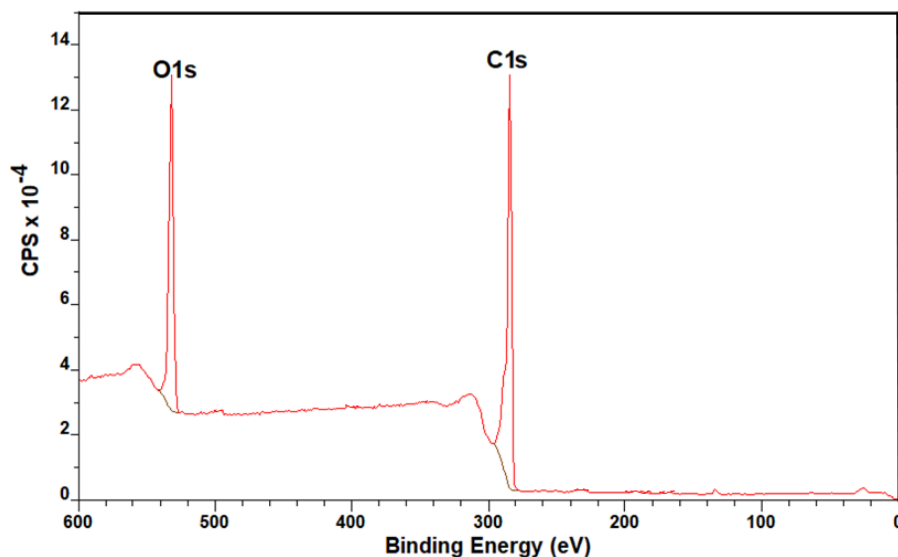


Figure 9.5: XPS survey scan of f-CLCNOs presenting the two major peaks for carbon and oxygen.

The deconvoluted C1s peak presented different types of C atom bonded to other atoms. The signals obtained comprised C atoms that are sp^2 and sp^3 hybridized as shown in **Figure 9.6** [53, 54]. The results in **Figure 9.6(a)** presents the presence of C-C, sp^2 -C, N- sp^3 -C or sp^3 -C, C-O and O-C=O which were indicated by the peaks positioned at 283.9 eV, 284.1 eV, 285.0 eV, 285.9 eV, and 288.7 eV respectively. About 48% of C-C were present in f-CLCNOs along with C-O as the dominating carbon bonding configurations.

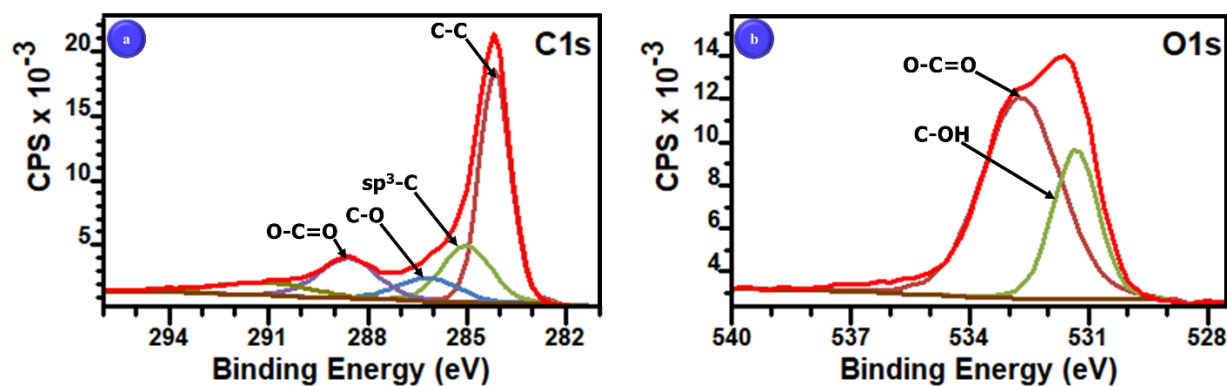
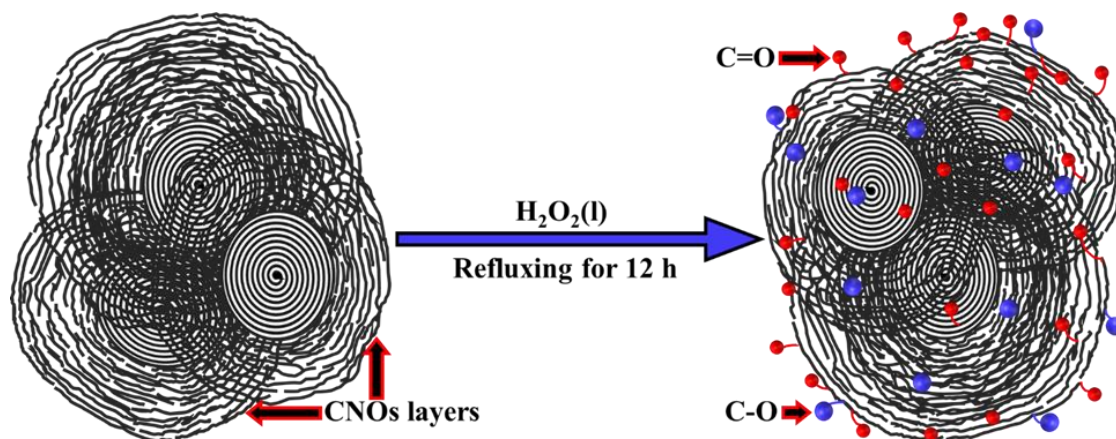


Figure 9.6: XPS survey scan of the deconvoluted f-CLCNOs spectrum; (a) C1s, and (b) O1s.

The O1s peak was also deconvoluted which confirmed that f-CLCNOs exhibit oxygenated carbon atoms with different bonding configurations as shown in **Figure 9.6(b)** [55]. Hence, the nanoparticles produced exhibited different oxygen species on their surfaces [55, 56]. The

deconvoluted O1s peak further indicates that most of the oxygen atoms are bonded to the carbon atoms with C-OH as well as O-C=O bonding configurations that are indicated by the peaks positioned at 531.1 eV and 533.5 eV respectively (see **Figure 9.6(b)**) [55, 56]. Moreover, about 14.7% and 10.5% of C-OH and O-C=O were present in the structural matrix of f-CLCNOs respectively. Thus it can be suggested that the surfaces of CNOs were dominated by oxygen-carrying functional groups (e.g. C_n-C=O) as described in **Scheme 9.2**.



Scheme 9.2: Introduction of functional groups on the surface of multi-shelled CLCNOs.

The Raman spectroscopy results confirmed that f-CLCNOs exhibit carbonaceous properties with the appearance of the D-band positioned in the expected Raman region between 1335 and 1345 cm⁻¹ as shown in **Figure 9.7(a)**. This observation can be ascribed to the increased disorder induced by C-C vibrations that correspond to the disruption of the sp² hybridized carbon bonds. The suggested disruptions are due to the presence of mainly the introduced oxygen-carrying functional groups, dangling bonds, sp³ bonding, intercalated C and H adatoms, vacancies, as well as other carbon rings arising from structural conformations [57, 58]. In addition, the presence of this D-band further indicates the breathing mode of the six-fold aromatic rings in the carbon nanoparticles structural matrix and [57, 59]. Moreover, the observed peak around 1585 cm⁻¹ is labelled as the G-band which is mostly ascribed to the C=C graphite carbon in-plane vibration modes of the carbon material with sp² orbital structure [60, 61]. The presence of the both bands (i.e. D- and G-band) lead to the quantification of f-CLCNOs graphitization degree which is basically the ratio of the areas (fitted with Voigt line shapes using the Origin 8.5 inbuilt fitting fixture) of the D-band to that of the G-band (I_D/I_G) was estimated (see **Figure S9.1**).

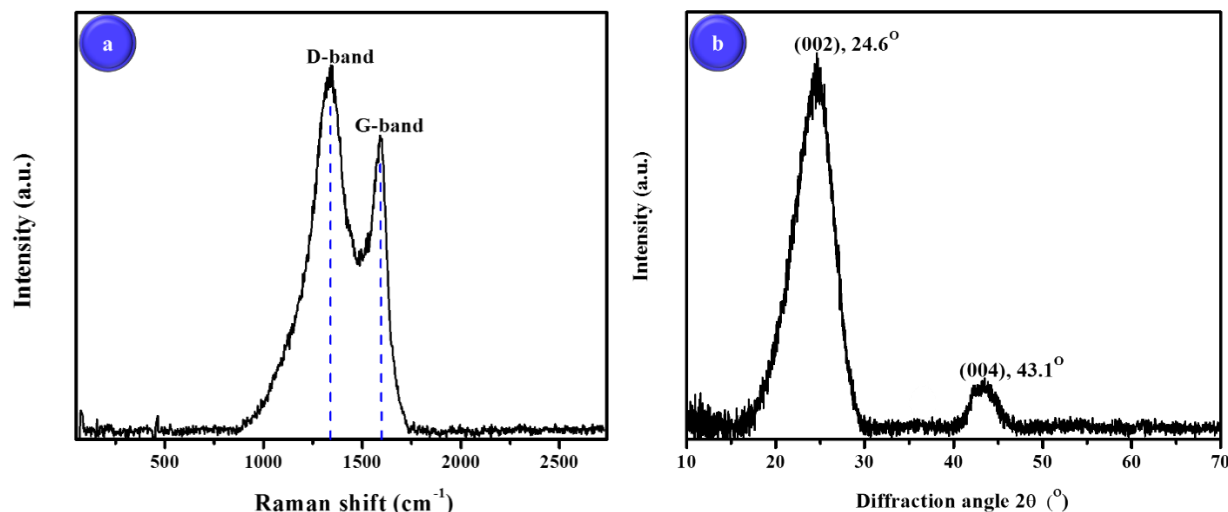


Figure 9.7: (a) Raman spectra of f-CLCNOs, and (b) PXRD patterns of f-CLCNOs.

It is best known that the defects and/or disorder density ratio (I_D/I_G) are directly related to the extent of disorder in the form of sp^3 hybridized carbons and the presence of either longer or shorter graphitic fragments [57, 59, 61]. It was obtained that the I_D/I_G value of f-CLCNOs is greater than 0.5 (i.e. $I_D/I_G = \text{ca. } 3.76$) which further denotes a moderate graphitized f-CLCNOs due to the presence of deformed graphitic carbon. This also suggests that f-CLCNOs exhibit a higher quantity of sp^3 to sp^2 carbon content since the spectrum shows a higher D-band intensity than that of the G-band (see **Figure 9.7(a)**). In addition, the obtained D-band full width at half maximum (FWHM) was higher than that of the G-band since they were found to be ca. 243.5 and 84.9 respectively. This indicates an increased amount of structural disorder that can be ascribed to the exposure of the in-plane terminations of either pentagonal or hexagonal carbon network with the surface functional groups of the f-CLCNOs as well as amorphous carbon impurities.

As shown in **Figure 9.7(b)**, the P-XRD pattern for f-CLCNOs presents the two prominent peaks for polycrystalline carbon material around 25° and 43°. These peaks can be assigned to the 002 and 004 planes of carbon nanoparticles. Thus, the appearance of peak centred at $2\theta \approx 43^\circ$ signifies that f-CLCNOs contain moderate graphitic carbon domains.

Interestingly, the obtained thermogravimetric analysis (TGA) and differential thermogravimetric analyses (DTA) data are in agreement with the Raman spectroscopy and TEM data. It is evident that f-CLCNOs decompose to completion (0% sample residue) since the carbons residual mass

remains at 0% following the completion of the TGA analysis as shown in **Figure 9.8(a)**. Thus, the obtained TGA profiles suggest rapid oxidative decomposition of the material following the on-set decomposition temperature mainly occurring around 592 °C [62].

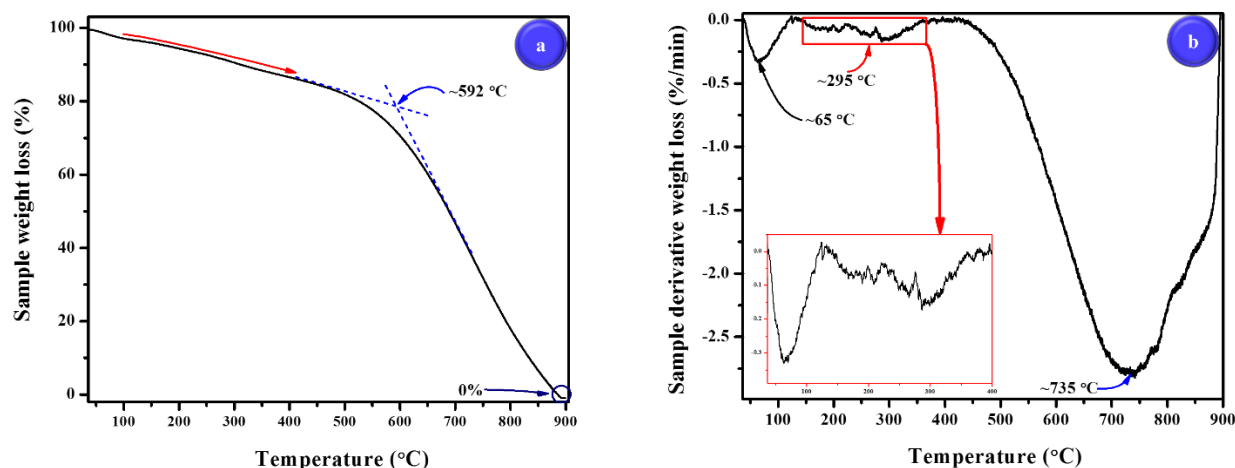


Figure 9.8: (a) thermogravimetric analysis profiles of f-CLCNOs, (b) first-order derivative weight loss curves of f-CLCNOs.

The first-order derivative weight loss curves for f-CLCNOs was also established as shown in **Figure 9.8(b)**. The first-order derivative weight loss (FDW) curve for f-CLCNOs exhibited a broader peak positioned around 735 °C. However, there existed the presence of peaks appearing between 50 and 400 °C. Notably, a peak around 60 °C signified further removal of minimal moisture content in the f-CLCNOs sample (see insert in **Figure 9.8(b)**). Moreover, the peaks positioned between 200 and 400 °C suggests the removal of multiple surface functional groups as well as the loss of amorphous carbon contents. The broader FDW curve positioned around 735 °C showed that the decomposition of this material happens in multiple stages. Following the observed morphology through TEM results, it can be suggested that there exist the first decomposition of the disordered concentric layers (e.g. outer shells) which occurs slowly. This is later followed by the decomposition of multiple graphitic carbon cores which were formed through the conglomeration of nanoparticles and exhibited by f-CLCNOs [63, 64].

The surface properties (i.e. the surface areas (SA) and pore sizes (PS)) of the f-CLCNOs were investigated using the BET surface characterization technique. The surface area was obtained as $103 \pm 0.13 \text{ m}^2/\text{g}$ in which the increased content of adatoms and/or functional groups possibly improved the surface area of the f-CLCNOs. Furthermore, the pore size and volume that f-

CLCNOs was found to be 41 nm $12.3 \text{ cm}^3/\text{g}$ and this could be as a result of inter-and intra-particle pores. In summary, the BET results indicate that the surface properties of the f-CLCNOs (i.e. the surface area, pore size and volume) are greatly influenced by their surface characteristics in which they greatly affect direct contact area (aggregation or agglomeration), the curvature, and shapes of carbon nanoparticles formed.

9.5. Electrochemical tests for VOCGs based on different CLCNOs

9.5.1. Signal to noise and resistance measurements of the sensing devices

Four different analytes; acetone, chloroform, ethanol and toluene were detected using a sensor that was fabricated with f-CLCNOs/MONR/PVP composite (i.e. sensor labelled as f-S). The signal to noise ratio (SNR) was determined using **Formula 2** discussed in **Section 5.2.4** in which different working frequencies were used (i.e. 1 kHz, 3 kHz, 6 kHz, 10 kHz and 20 kHz). The sensing device had the highest SNR value exists at 3 kHz relative to the frequency working range as shown in **Figure 9.9**. Therefore, 3 kHz was selected as the optimal working frequency for all test measurement conducted. The use of 3 kHz as the operating frequency was preferred because it also allowed for the fabrication of a sensing system that suggests less electrical power consumption [65].

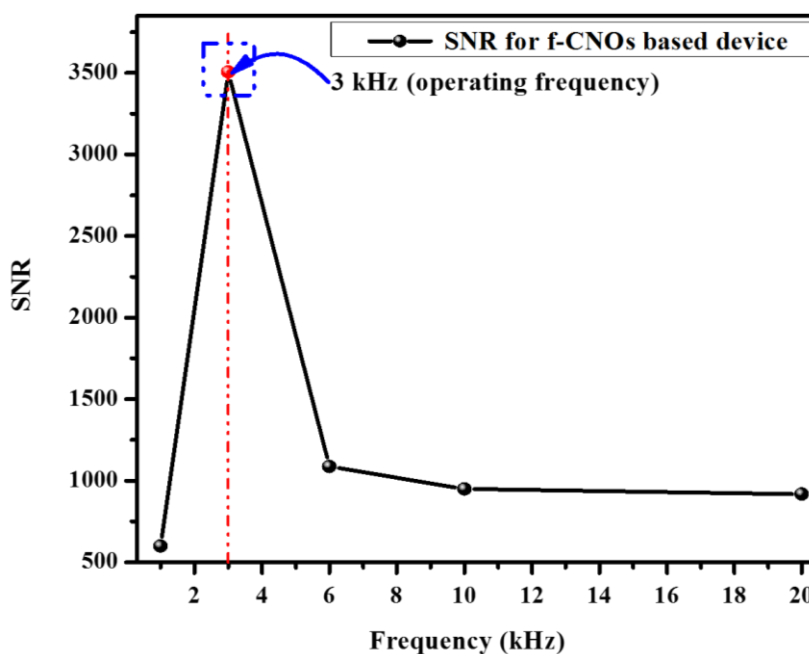


Figure 9.9: SNR plot that represents sensor's highest response at 3 kHz.

A similar response was shown by the decrease in resistance with an increase in the concentration of all analytes as shown in **Figure 9.10**. Whenever the n-type semiconducting metal oxide is used in gas sensing fabrication, negative charge carriers dominates as the majority charge carriers. Their presence mostly increases the conductivity whenever a reducing gas (i.e. electron donor) is detected [66]. Thus, since the sensing composite contains MONRs, it is evident the resistance of the sensor decreases as the concentration of different analytes increases as shown in **Figure 9.10(a-d)**. This trend suggests that the detected analytes exhibit properties such as organic functional groups that facilitate molecular interaction with the n-type MONRs.

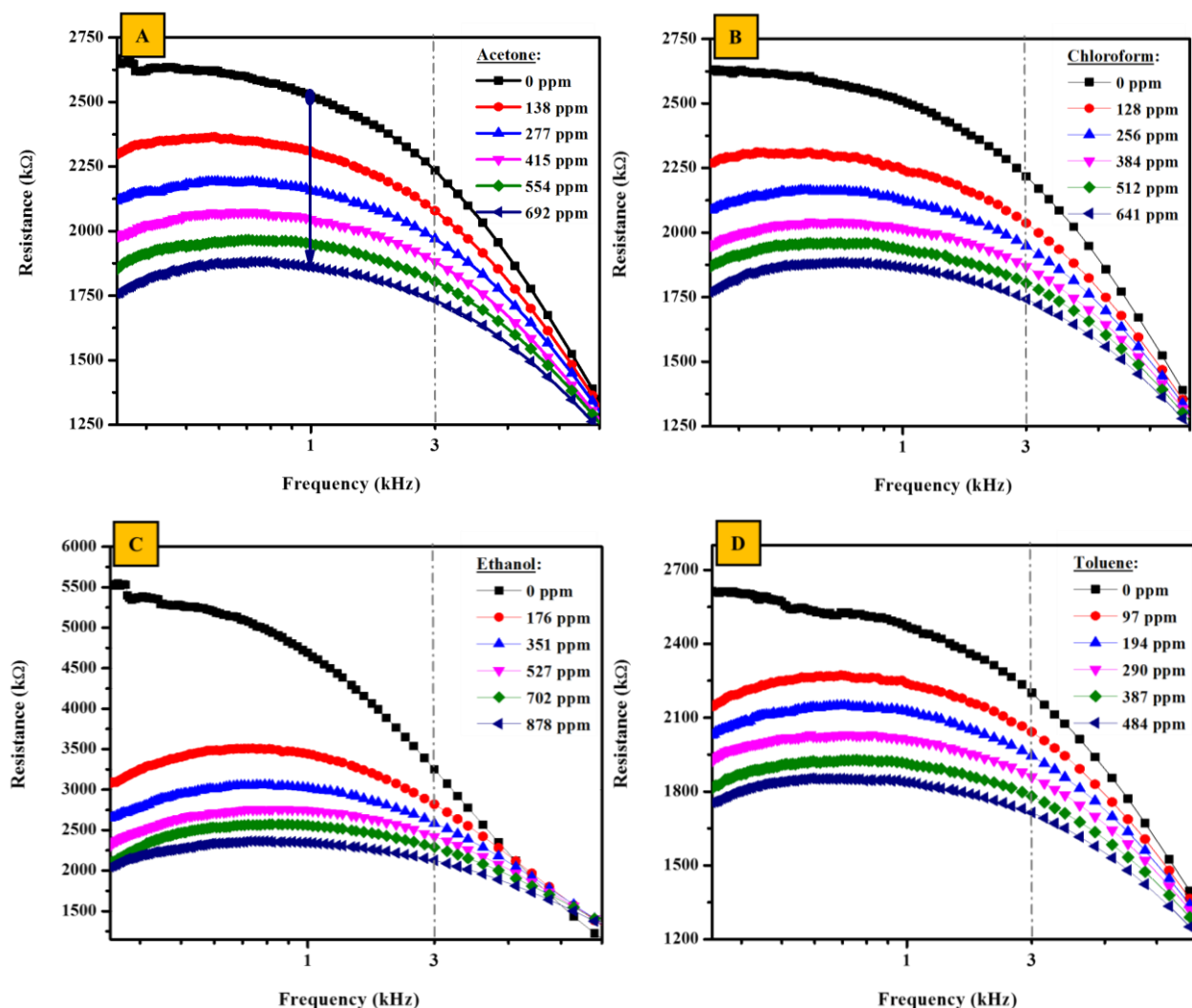


Figure 9.10: Plots of resistance (R in $k\Omega$) as a function of frequency for detecting; (a) acetone, (b) chloroform, (c) ethanol, and (d) toluene, at varied analyte concentrations respectively.

Moreover, it can also be suggested that all analytes are capable of donating electrons to the active sensing material which result in increased charge carriers within the sensing layer. Interestingly, it was also identified that the response towards the four analytes presented an alternating change in resistance as shown by arrows facing down and up in **Figure 9.11(a-d)**. Moreover, the shape of the baselines for the blank measurements was also identical in all cases. With the measurements of response ($\Delta R/R_0$) as a function of frequency, the results obtained suggest that the adsorption of different analyte molecules on a carbon-based sensing material selectively depends on several parameters such as the dipole-moment and the porosity of the carbonaceous surface that is present in the sensing composite [67].

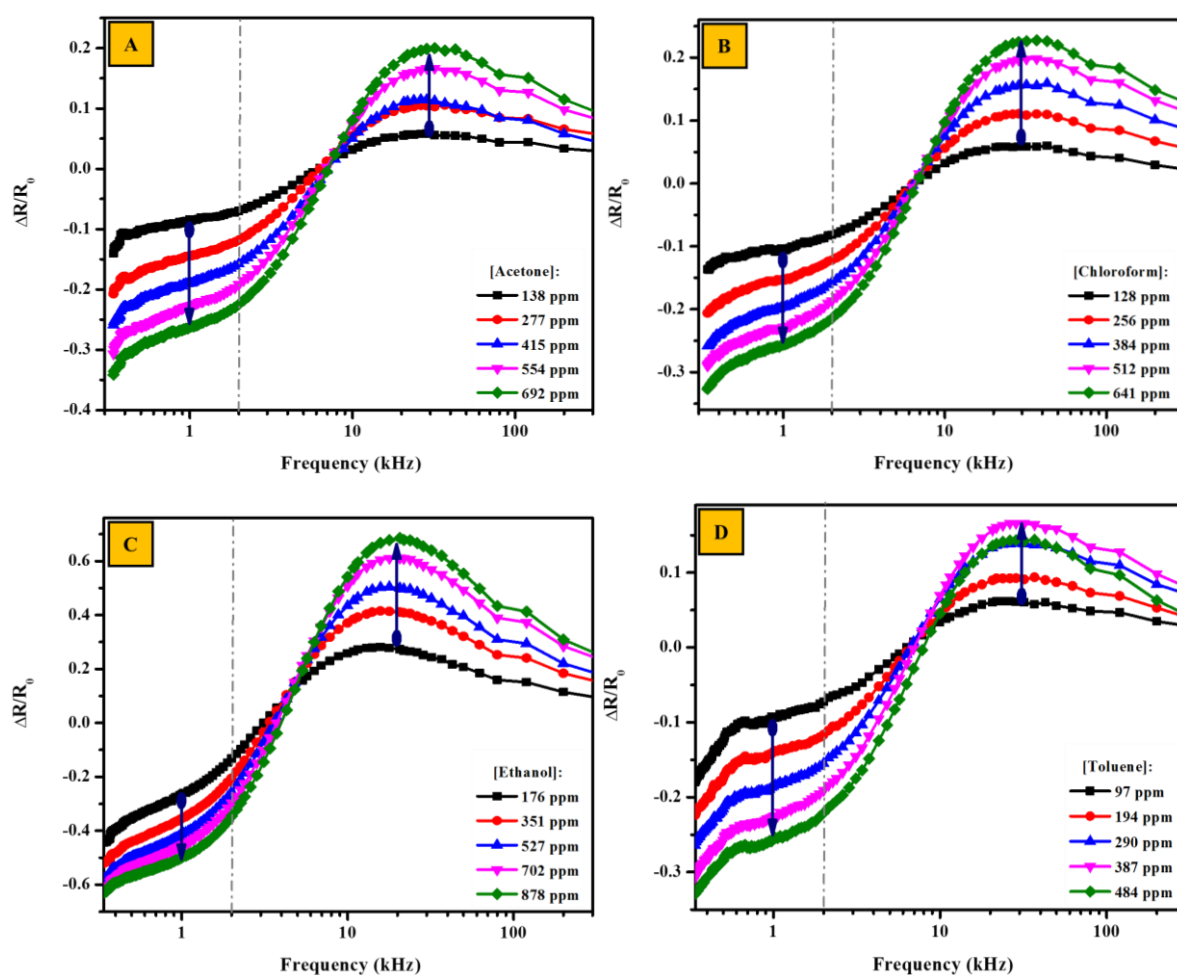


Figure 9.11: Plots that indicate the sensor's response ($\Delta R/R_0$) towards varied analyte concentrations as a function of frequency for detecting; (a) acetone, (b) chloroform, (c) ethanol, and (d) toluene.

It was further noticed that the relative resistance decreases as the concentration of the analyte increases whenever the sensor is operated between 0.3 and 7 kHz, for all analytes tested. This trend suggests that the active sensing composite acts as an n-type sensing material whenever the device is operated at lower frequencies (i.e. <7 kHz). Alternatively, the resistance increases as the concentration of the analyte increase whenever the device is operated between 7 and 20 kHz in all cases. This suggests a p-type sensing behavior towards all analytes attributed to the presence of electrons that provide a stronger electron-accepting interaction with the adsorbed oxygen ions on the surface of the MONRs-based sensing material [68].

Moreover, it was also suggested that the trapped electrons on the sensing material's surface are reverted during the redox reaction that occurs [69-71]. For example, the ionic species such as Cl^- and OH^- from chloroform ($\text{CH}_3\text{-Cl}$), as well as ethanol ($\text{CH}_3\text{CH}_2\text{-OH}$) molecules, can interact with the sensing material through an electron-donating effect resulting in enhanced charge carrier mobility (i.e. decrease in resistance and increase in conductivity). On the other hand, a similar electron-donating effect can occur due to the presence of carbonyl groups and the aromatic mono-substituted benzene rings from acetone ($\text{CH}_3\text{-CO-CH}_3$) and toluene ($\text{C}_6\text{H}_5\text{-CH}_3$) respectively. This is possible since the carbonyl group from $\text{CH}_3\text{-CO-CH}_3$ carries an electron-rich oxygen species whereas the aromatic ring from $\text{C}_6\text{H}_5\text{-CH}_3$ is capable of providing the $\pi\text{-}\pi$ electrons [72, 73]. This is an interesting behavior that suggests that this kind of sensing composite can be used to respond towards the four analytes as either an n-type or p-type active sensing material depending on the operating frequency [74].

In summary, the results show that at 3 kHz the response ($\Delta R/R_0$) decreases as the concentration of the analytes used increases which can be attributed to the active sites that are on the surfaces of the f-CLCNOs/MONRs/PVP composite. It should be noted that the surface functional groups on f-CLCNOs can also facilitate the electron exchanges during the chemical interaction between the analyte and the entire sensing composite. In addition, some of the surface active sites can be provided by the semiconducting MONRs. Thus, it can be said that the ionized surface attached species are also responsible for breaking down every analyte's molecule to adsorb any available electron-donating.

Depending on the molecular structure of every polar aprotic analyte, they can be regarded as molecules that are incapable of donating protons in hydrogen bonding interactions [75]. However, they are mostly capable of donating electrons which are important for every analyte's detection.

Considering the f-CLCNOs-based sensing material used in this study, it is also significant to note that the presence of carbon embedded MONRs in the sensing composites provides the n-type semiconducting properties in which electrons are available as major charge carriers in the system containing a reducing gas. Thus, MONRs in the sensing composite provides different oxygen species including O_2^- (superoxide) which rarely exists in carbonaceous materials such as in f-CLCNOs [76]. f-CLCNOs exhibit different types of oxygen species except for the superoxide species, which means that the MONRs in the sensing composite synergistically provide superoxide species for better gas sensing properties towards different analytes [77]. Furthermore, it can be suggested that the detection mechanism depends on the availability of electron donating groups on the analyte's molecules similar to the discussed mechanism in **Section 6.5.1**.

In summary, the composites used in this study reveal the synergistic effects between all materials used in the mixture (i.e. f-CLCNOs, MONRs, PVP). The obtained results suggest that the response of the sensors is greatly influenced by simultaneous surface interactions of the analyte's gas molecules with f-CLCNOs and/or MONRs. However, this depends on the availability or exposure of active adsorption sites which can also be influenced by dispersion and film thickness of the active sensing material as well as the flexibility to actively work at room temperature.

9.5.2. Sensitivities (S), limit of detections (LoDs) and time related studies of the sensing device

Following the confirmation that the device gives an n-type behavior towards the four analytes, further investigation was done on the sensitivity of the sensor (f-S) under the decreasing resistance and SNR conditions (i.e. at 3 kHz for varied analytes concentrations (ppm) respectively). The results in **Figure 9.12** and **S9.2** reveals different sensitivities (S) toward the four analytes that were used. It can be seen that the sensor is the most sensitive toward toluene and the decreasing order of sensitivities is; toluene $S_{toluene}$: $3.16 \times 10^{-4} \text{ ppm}^{-1}$ $>$ $S_{acetone}$: $2.23 \times 10^{-4} \text{ ppm}^{-1}$ $>$ $S_{ethanol}$: $2.03 \times 10^{-5} \text{ ppm}^{-1}$ $>$ $S_{chloroform}$: $1.99 \times 10^{-5} \text{ ppm}^{-1}$ as shown in **Figure S9.2**. The type of electrons (i.e. π - π electrons) present in toluene is easily donated onto f-CLCNOs-MONRs-based surface that is also electron-rich.

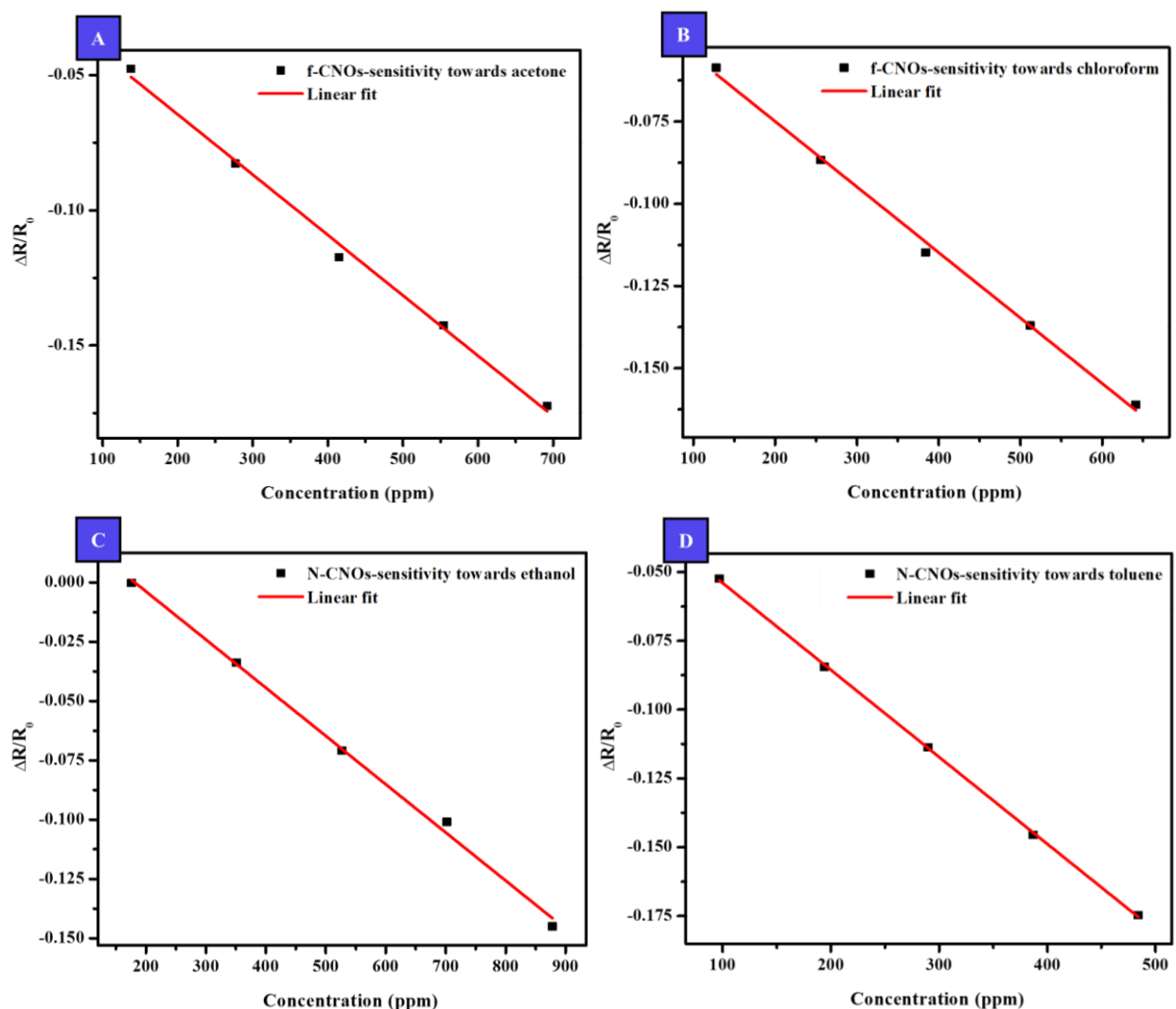


Figure 9.12: Sensor's response ($\Delta R/R_0$) operating at 3 kHz as a function of varied analytes concentrations with the slopes of the calibration curves for detection of; (a) acetone, (b) chloroform, (c) ethanol, and (d) toluene.

The lowest amount of every analyte that is significantly different from the blank in the sensing system was determined using the LoD formula (see **Section 5.2.4**). As shown in **Figure 9.13** and **S9.3**, the LoD results for all analytes tested indicates that the analyte with the lowest LoD is toluene (LoD: 1.48 ppm). This is in correspondence with the sensitivity results since it is found that the sensor is mostly sensitive for detecting toluene while being capable of identifying its molecules at lower concentrations (i.e. <2 ppm). Furthermore, the summary in **Figure S9.3** also reveals that as the sensor is mostly sensitive towards toluene, it also has the lowest LoD (i.e. 1.48 ppm). As such, this kind of device is best suitable for detecting toluene at room temperature. The observed sensing

behavior towards toluene can be attributed to the presence of easily available electron-donating groups that are easily generated and rapidly interact with the active sites on the f-CLCNOs/MONRs/PVP composite surface edges. In addition to the LoD results, the sensor's response and recovery duration was also investigated for every analyte.

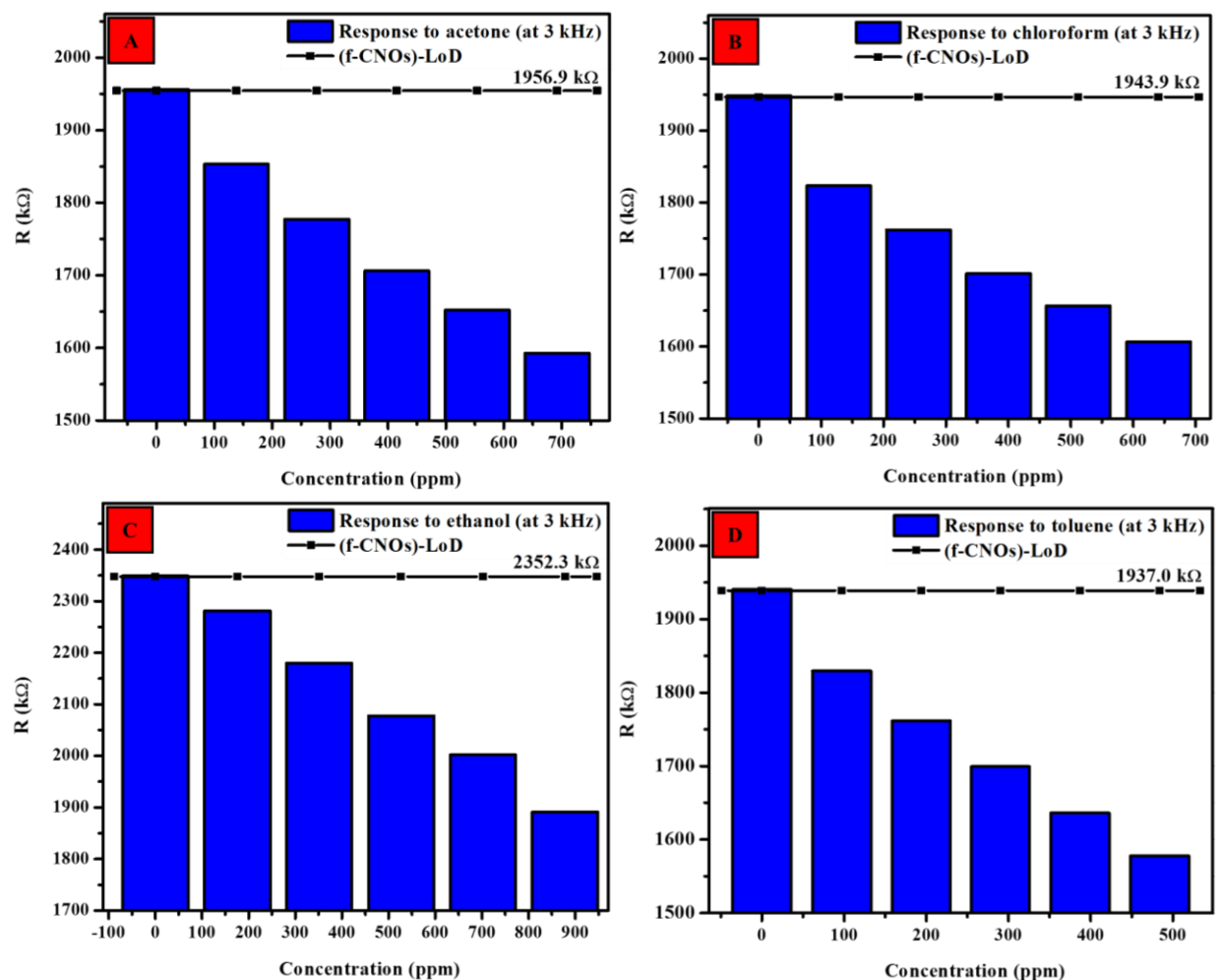


Figure 9.13: Resistance at 3 kHz as a function of analyte concentration, the black horizontal line indicates the estimated LoD towards the detection of; (a) acetone, (b) chloroform, (c) ethanol, and (d) toluene.

The speed at which the sensor detected each analyte and the readiness to measure it again was an important dynamic characteristic of the sensor's performance [78]. This type of measurement indirectly shows the adsorption dynamics of the analyte molecules by the active material, from the non-interaction state up to the dynamic equilibrium [78]. The results in **Figure 9.14** also reveal

that all analytes interact with the sensing material as shown by the change in resistance with increasing time.

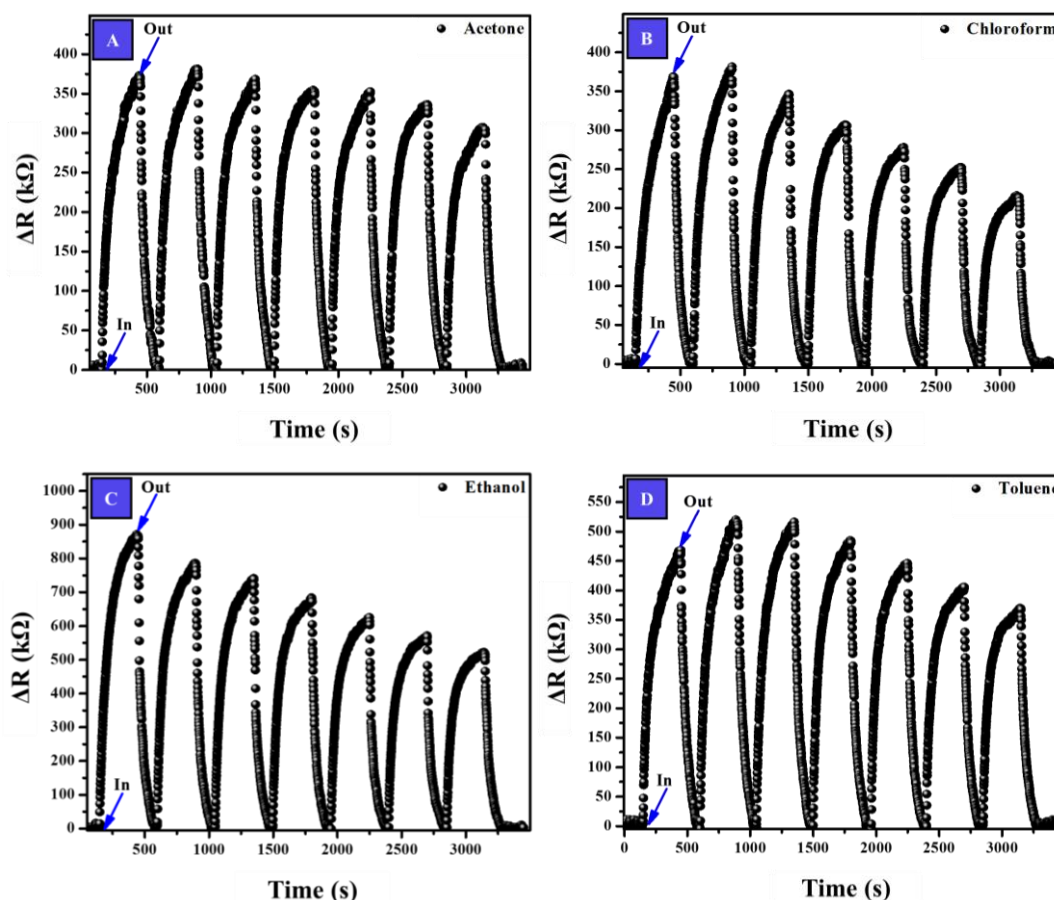


Figure 9.14: Response and recovery time measurement plots obtained during the detection of; (a) acetone, (b) chloroform, (c) ethanol, and (d) toluene following an increasing 1 μL injection intervals.

It can be seen that the sensor responds quicker towards ethanol (at 171s) with the second most recovery time as shown in **Figure 9.15**. This device has a faster recovery time towards chloroform (at 69s, also see **Figure 9.15** and **S9.4**). The observed time-related trend depends on the molecular interaction between the analyte's molecules and the sensing composite. In each case, the analyte molecules adsorb on the surface of the sensing composite and rapidly occupy any active sites increasing the charge carrier density (i.e. increasing conductivity) which result in the relative resistance to decrease with time [79, 80]. Moreover, the molecular sizes of every analyte's molecules along with their volatility contribute towards the estimated response and recovery times.

In addition, it was also noticed that the saturation or steady-state of the sensor appeared to range from 55s to 95s depending on the analyte (e.g. chloroform: ~57s and toluene: 92s, see **Figure 9.15**).

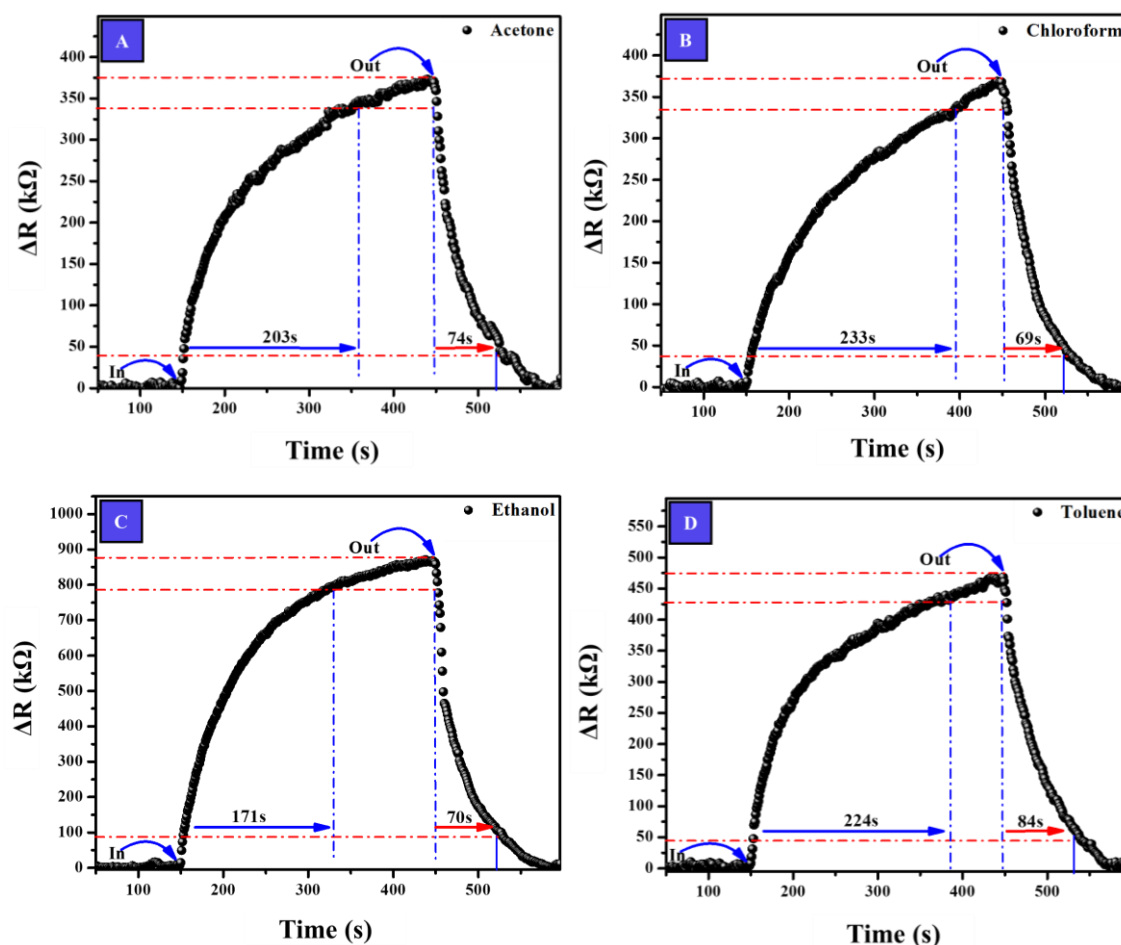


Figure 9.15: Zoomed (between 150s and 600s) response and recovery time measurement plots obtained during the detection of; (a) acetone, (b) chloroform, (c) ethanol, and (d) toluene for the first 1 μL injection.

9.6. Conclusions

A facile synthesis of quasi-spherical CNOs with particle sizes of ca. 55 nm was successfully achieved using the olive oil flame pyrolysis process. Upon functionalization of CLCNOs, the defect density in the CLCNOs structural matrix increased. The presence of CLCNOs structural defects and/or disorder was confirmed by the broader first-order derivative peak (i.e. DTA data) as well as the Raman band area I_D/I_G ratio=3.76. The surface areas of f-CLCNOs was greater than 100 m^2/g and can be directly related to the surface functional groups introduced by hydrogen

peroxide as revealed by the FTIR and XPS results. It was observed that the sensor can be used at different operating frequencies in order to study its n- or p-type sensing behavior. Significantly, the f-S sensor exhibited higher sensitivity towards toluene with the lowest LoD. The obtained data indicated that the physicochemical properties of the materials used to form the composites (i.e. f-CLCNOs, MONRs and PVP) influence the response of the sensing device towards the detection of various VOCs at room temperature. In addition, the sensor's dynamic characterization showed that the response and recovery times for detecting the four analytes are slightly different with few seconds. However, the investigation revealed that the sensor responded faster towards ethanol (171s) in which the recovery time was 70s to recover to its initial sensing state. Thus, there is great potential to improve the chemical sensing properties using different composites of carbon nanoparticles, such as functionalized CLCNOs, and various metal oxide nanoparticles.

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CHAPTER 10

General conclusions and recommendations

10.1. Introduction

In this research project, the main aim was to optimize the synthesis parameters for the production of pure CLCNOs in high yields using a simple flame pyrolysis method. Coconut oil, cod-liver oil, olive oil and sweet oil were selected as the carbon sources and/or precursors. CLCNOs were doped with heteroatoms and functionalized to understand the effect of additional functional groups or heteroatoms on their surface properties towards gas sensing. A number of VOCs were tested using gas sensors fabricated with different CLCNOs, Mn_2O and PVP. In particular, acetone, ammonia, chloroform, ethanol and toluene were tested using chemiresistive sensing devices at room temperature. The dynamic and static characterization were achieved by using the LCR meter.

As such, insights into CLCNOs facile synthesis have been highlighted, and an innovative gas sensing method has been developed for basic detection of sensing various VOCs. Therefore, the following conclusions and recommendations were drawn following the collective results obtained.

10.2. General conclusions

10.2.1. Synthesis of CLCNOs using different oils as carbon sources

CLCNOs with short range ordered multi-layers were successfully synthesized using an inexpensive and simple open flame pyrolysis method (OFP) using four different essential oils as carbon sources. TEM micrographs revealed that core-filled CLCNOs were produced with an average particle sizes that are less than 70 nm. With the use of different oils, the obtained quasi-spherical nanomaterials exhibited similar physicochemical properties. Hence, it can be suggested that CLCNOs synthesis using OFP is independent of the oil used in this study during their production process. Moreover, these polycrystalline and surface fragmented materials can be used in various applications since they can be produced in large amounts. This are interesting properties that prompted further investigations of applying CLCNOs from a selected oil precursor in toxic gas sensors

10.2.2. The use of olive oil derived CLCNOs in chemiresistive gas sensors

Olive oil derived CLCNOs (p_{oli} CLCNOs) were synthesized to study their surface organic oxygen carrying functional groups (e.g. carboxylic groups) they exhibit. The materials were defective and used as chemiresistive gas sensing material due to their surface features. It was noted that they provide additional electrical properties such as allowing the ease of charge carrier mobility when they are used in a composite made of MONRs and PVP. This observation revealed an important synergy between the three materials. Moreover, basic static characteristics obtained after detecting acetone, chloroform, ethanol, toluene using the p_{oli} CLCNOs/MONRs/PVP composite based sensors revealed that the composite favored the detection of chloroform as compared to other VOCs. Following these observations, it can be said that p_{oli} CLCNOs exhibited unique and important chemical and physical properties that allowed the synergistic activity between the three materials in the p_{oli} CLCNOs/MONRs/PVP sensing composite.

10.2.3. Comparison study between the ex-situ nitrogen doped olive oil derived CLCNOs and as-synthesized olive oil derived CLCNOs for application in acetone detection

With the aim of detecting acetone, various gas sensing composites were successfully prepared using the as-synthesized and doped CLCNOs. It is important to mention that the doping parameters (e.g. dopant flow rate) play a significant role for making higher nitrogen content on CLCNOs surfaces. Notably, doping CLCNOs increased the total surface area of the materials which is essential for gas sensing application purposes. Therefore, the results confirmed that acetone can be detected using a gas detector fabricated with nitrogen doped CLCNOs (at 100 sccm of ammonia) and a MONRs-based composite. In fact, this was the most sensitive composite for detecting acetone at room temperature although the limit of detecting acetone was higher than that of the as-synthesized CLCNOs/MONRs/PVP composite. Thus, the composites play an important role in fabricating portable gas sensing devices that can be utilized to detect acetone at room temperature.

10.2.4. Application of in-situ nitrogen doped CLCNOs in chemiresistive gas sensors for detecting three different VOCs at room temperature

Dense CLCNOs were in-situ doped with nitrogen to form N-CLCNOs using pyridine as the source of carbon and nitrogen. As such, the quasi-spherical N-CLCNOs with particle sizes ca. 69.6 ± 3.5 nm were dominated by pyridinic N atoms which presented interesting chemical behavior for the detection of acetone, ethanol and toluene. This material exhibited higher surface area (i.e. $294 \text{ m}^2/\text{g}$) and pore sizes (i.e. 3.18 nm) as compared to MONRs (i.e. $33.3 \text{ m}^2/\text{g}$ and 0.23 nm). With this type of N-CLCNOs characteristic, the sensing device fabricated with the N-CLCNOs/MONRs/PVP composite presented a low limit of detection and high sensitivity during the detection of toluene as compared to acetone and ethanol. However, the best sensor linearity was obtained during the detection of acetone at 3 kHz. Moreover, the dynamic chemiresistive characterization revealed that the device responded faster (i.e. in 204 s) towards ethanol with a recovery time of 72 s as compared to other analytes used in this study. Therefore, it is suggested that this type of composite be used as one of the active sensing material.

10.2.5. The selective study of response and recovery times of various volatile organic chemical gas sensors fabricated using different carbon nano-onions

CLCNOs were used as one of the materials to make different gas sensing composites. The defective CLCNOs were successfully used to fabricate pCLCNOs/MONRs/PVP- and a_{oli}CLCNOs/MONRs/PVP-based sensors for detecting acetone and ammonia. An investigation to detect both analytes at room temperature was carried-out through dynamic chemiresistive studies. The sensors' response and recovery times were determined in which a_{oli}CLCNOs/MONRs/PVP-based sensor responded faster toward acetone and ammonia although it recovered slower than the pCLCNOs/MONRs/PVP-based sensor. In both cases, the sensing devices presented n-type and p-type sensing characteristics when used to detect acetone and ammonia respectively. Therefore, this alternating sensing behavior is ascribed to the surface chemical interaction that takes place between the analyte molecules and the sensing composite. As such, it is important to use both types of composites to detect various VOCs at room temperature.

10.2.6. The study of functionalized carbon nano-onions and its metal oxide containing composite for application in chemiresistive gas sensors

Most studies report on the importance of surface functional groups on most carbonaceous nanoparticles. In this study, investigations on the addition or introduction of surface functional groups on olive oil derived CLCNOs through the use of H_2O_2 were carried out. The FTIR and XPS data confirmed the dominating presence of oxygen carrying functional groups (e.g. carboxylic groups) on the CLCNOs surfaces. Moreover, Raman spectras analysis revealed that the turbostratic f-CLCNOs structural architectures were highly defective and/or disordered since the calculated I_D/I_G was 3.76. The f-CLCNOs were successfully applied in chemiresistive sensors as a f-CLCNOs/MONRs/PVP composite. The dynamic and static characteristics of f-CLCNOs/MONRs/PVP-based sensors were obtained during the detection of acetone, chloroform, ethanol and toluene. The sensing device presented alternating sensing behavior (i.e. n- or p-type) depending on the operating frequency. It is capable of detecting toluene at a lower concentration. However, it responded faster towards ethanol (171 s) as compared to toluene. Hence, it shows better linearity when used to detect ethanol than in the case of other VOCs. Thus, f-CLCNOs can be used for preparation of carbon nanomaterial and metal oxide based composites that are useful in VOCs sensing devices.

Overall, this study demonstrated that through the selective use of essential oils, high quality CLCNOs can be produced. Functionalization and heteroatom doping enhanced the properties of these material. Thus, this makes them the best candidates for use in chemiresistive gas sensors.

10.3. General recommendations

With an increased desire to detect VOCs at room temperature using inexpensive, omni-sized and user-friendly gas sensors, further investigations and/or improvements in the three material (i.e. carbon nanoparticles, metal oxides and polymers) composites are required. The following is recommended:

- Synthesis of CLCNOs using combustible precursors that contains different heteroatoms such as boron and sulphur in order to improve their chemical and electrical properties.

- Study the structural re-arrangement of disordered CLCNOs layers by annealing them at elevated temperatures (i.e. >1200 °C) in an inert atmosphere.
- Direct metal decoration of CLCNOs with metal carbonyls such as manganese carbonyl ($C_{10}O_{10}Mn_2$) and cobalt carbonyl ($Co_2(CO)_8$) in order to further apply them in gas sensors as well as possible catalytic studies.
- Application of metal decorated CLCNOs in gas sensing devices through the use of thin layer coating or sputtering systems in order to monitor the film thicknesses.
- Verification of the suggested operation mechanisms using FTIR coupled with a LCR meter in order to understand the decomposition of most VOCs during their redox interactions with the sensing material.
- Design and use of an automated chamber system in order to further investigate the effectiveness of multiple CLCNOs-based composites with various metal oxide nanoparticles (e.g. TiO_2) to detect different VOCs.
- Exploration of controlling sensing layer/film thickness by employing the use of systems including sputtering physical vapor deposition method compared to the solution drop casting method that was used in this study.
- Investigation of long-term signal drift and stability of this type of sensing device as well as their sensing-layer-dependent reproducibility.
- Further understanding of selectivity and sensitivity for sensing devices that are fabricated with various composites composed of different CLCNOs, metal oxides and polymers by employing methods such as tristimulus analysis. This might allow for further exploration on functional 3-S parameters (i.e. selectivity, sensitivity and stability). Thus, the performance of this type of device in a humid environment can be better understood.

Given the kind of explorations and discoveries made in this project, it can be said that there is a great future potential to improve the chemical sensing properties of CLCNOs using different composites. The composites of interest can be based on other hetero-atoms decorated CLCNOs (e.g. sulphur doped CLCNOs), and various shaped metal oxide nanoparticles (e.g. ZnO) in order to understand the sensing properties of CLCNOs and different metal oxides-based composites at room temperature.

Appendix A: Supplementary Information



Figure S8.1: A photo that shows the LCR meter and glove box set-up used during the static characterization.

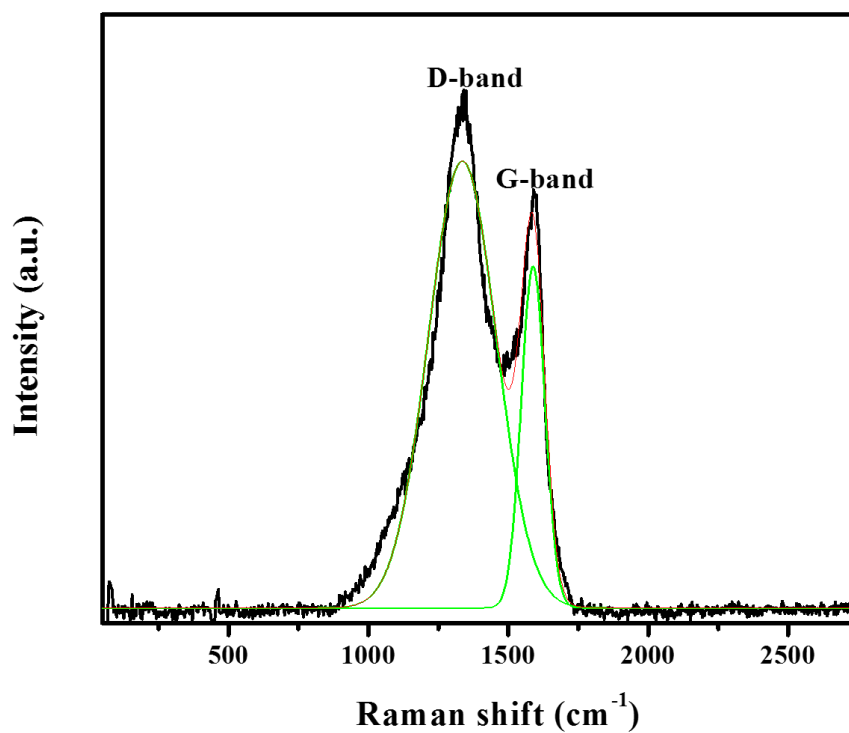


Figure S9.1: Raman spectra of f-CLCNOs with fitted D- and G-band.

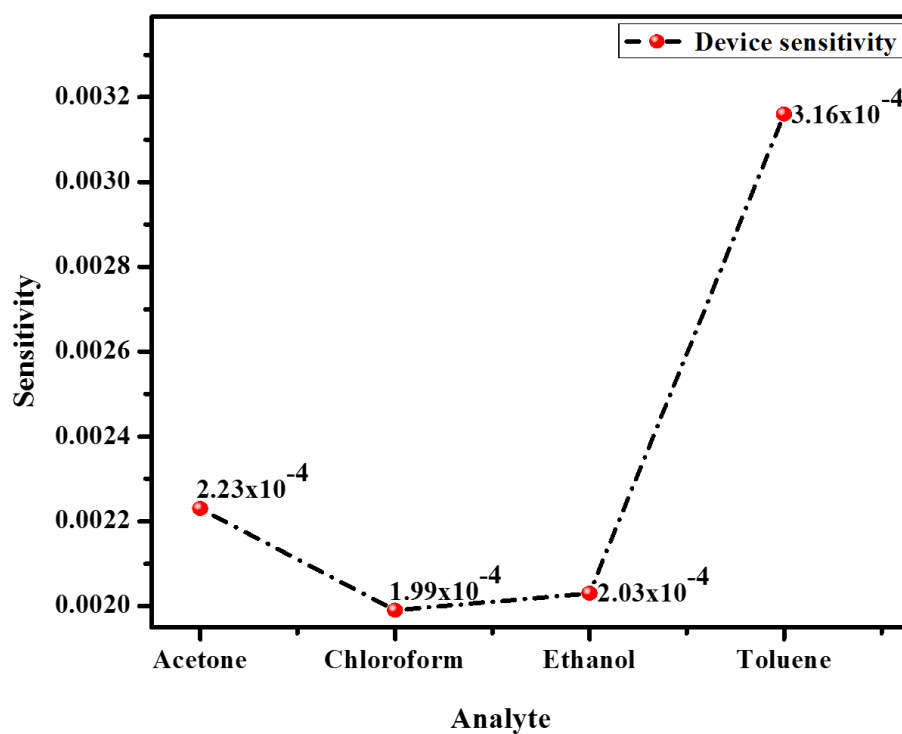


Figure S9.2: Sensitivity comparison plot for different analytes used in this study.

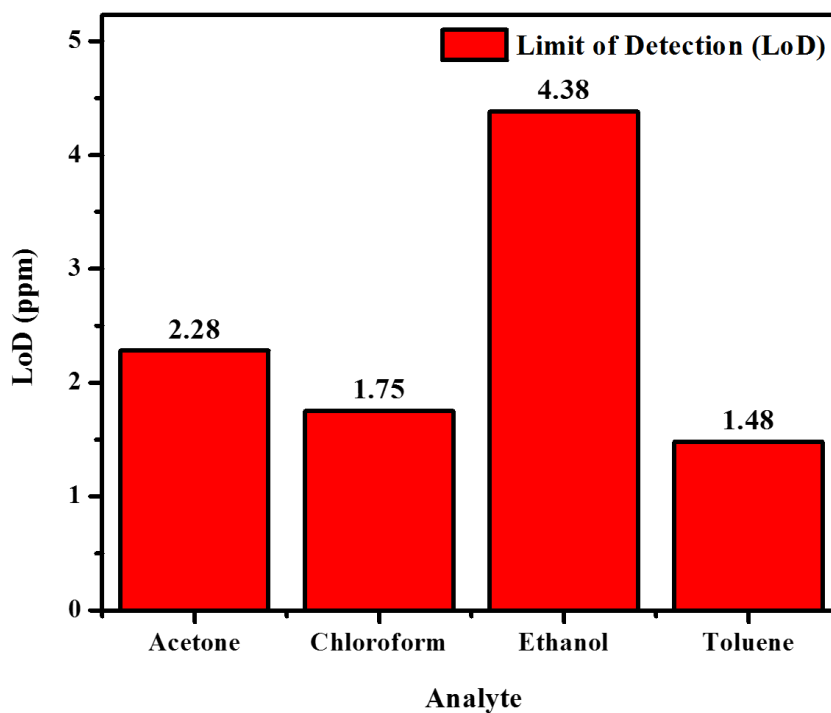


Figure S9.3: LoD comparison bar graph for the all analytes used in this study.

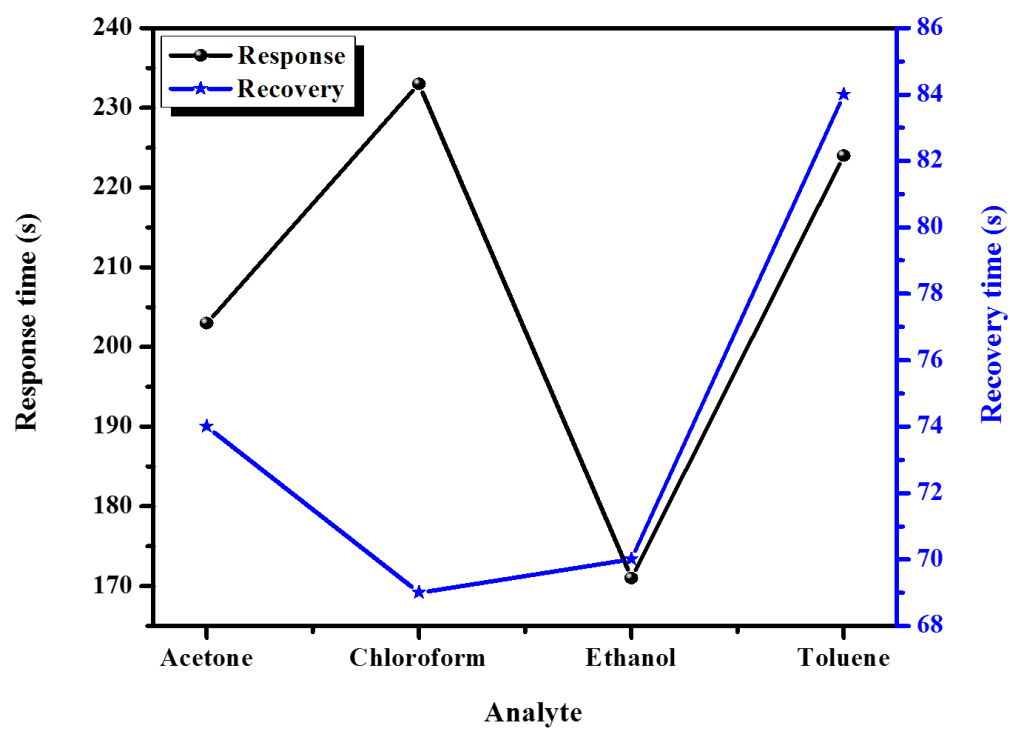


Figure S9.4: Comparison plots for the sensors' response and recovery times.